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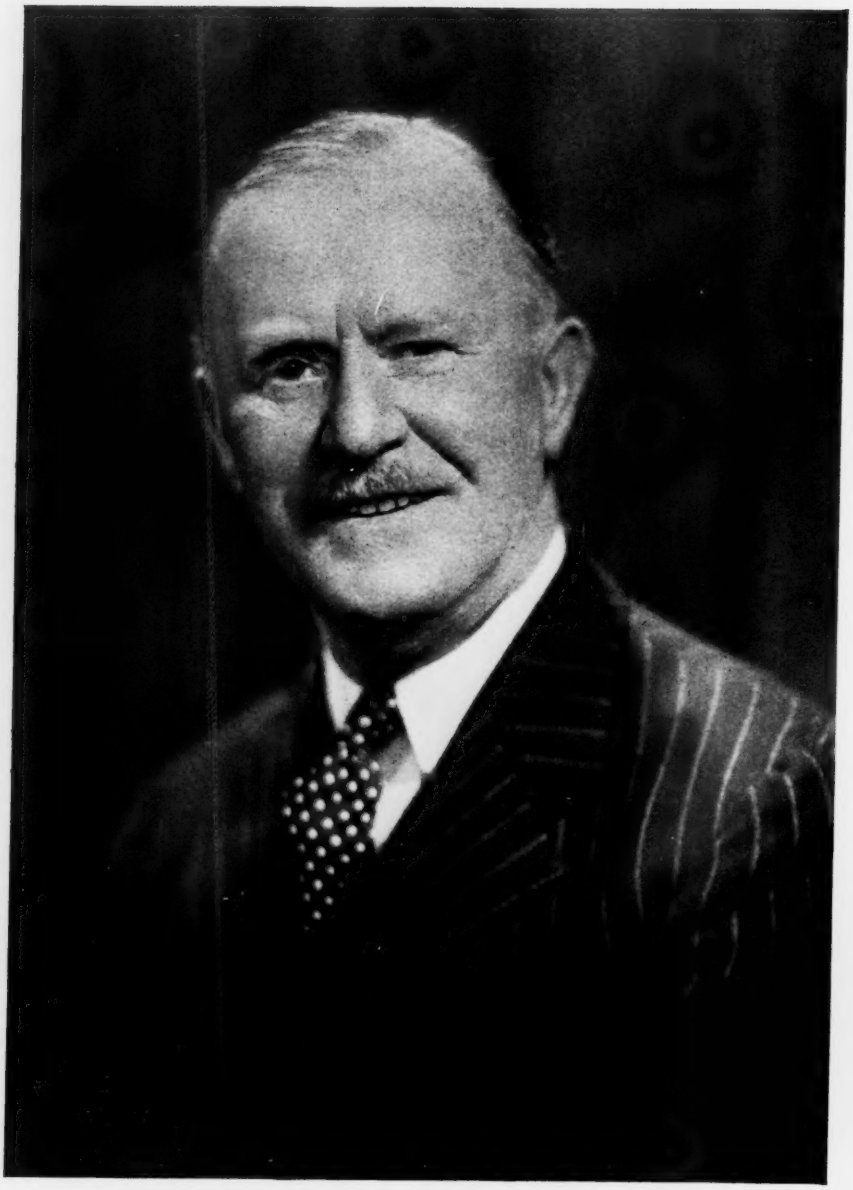
A. McKENDRICK, M.C.

ALEXANDER McKENDRICK was born and educated in Glasgow. He commenced his career in 1910 as a trainee with the Glasgow and South Western Railway. During the First World War he served in the Near East and in France, and was awarded the Military Cross in 1919.

On his return to civilian life, Mr. McKendrick joined the Lanarkshire Steel Company, Limited, Motherwell, as Welfare and Labour Officer. In 1923 he took up a similar appointment with Colvilles Limited, at the Clydebridge Steelworks, and in 1926 he became Traffic and Yard Manager. From 1929 to 1938 he was Traffic, Yard and Bricklaying Superintendent at Steel, Peech and Tozer Limited, Rotherham. He was then appointed Manager for Scotland for General Refractories Limited. He was appointed a Director of Glenboig Union Fireclay Company, Limited, in 1939, and Joint Managing Director, and finally Managing Director, in 1940. In the same year he was also appointed a Director of General Refractories Limited, and of Henry Foster and Company, Newcastle-on-Tyne.

Mr. McKendrick has been a member of the Lanarkshire District Committee for the Scottish Board for Industry since 1946, and was appointed Chairman in 1952. He has been a member of the Steelmaking Refractories Joint Committee of the British Iron and Steel Research Association since its inception. President of the West of Scotland Iron and Steel Institute for the session 1953-54, he was elected a Member of The Iron and Steel Institute in 1936.



A. McKendrick, M.C.

Honorary Member of Council, 1952-53

PROCEEDINGS OF THE INSTITUTE

REPORTS OF COUNCIL - OFFICIAL NOTICES

SPECIAL MEETING IN THE NETHERLANDS, 1953

A Special Meeting of The Iron and Steel Institute was held in the Netherlands from Wednesday, 30th September, to Wednesday, 7th October, 1953. The centre of the Meeting was in Amsterdam and visits to works and excursions were made in Amsterdam, and to Ymuiden, Delft, Rotterdam, and Utrecht.

An Opening Session was held at the Grand Hotel Krasnapolsky, in Amsterdam, on 1st October, at which two short lectures were given and a technical film was shown.

RECEPTION COMMITTEE

A Reception Committee, of which Mr. A. H. Ingen Housz, President van de Directie der Koninklijke Nederlandsche Hoogovens en Staalfabrieken, N.V., was Chairman, was formed in the Netherlands to make the necessary arrangements. A Ladies' Committee was also formed under the chairmanship of Mrs. Ingen Housz. Mr. C. F. van Dam, of the Royal Netherlands Blast-Furnaces and Steelworks, Ltd., helped in making many of the arrangements in the Netherlands.*

Groenburgwal, Amsterdam

The President and Council wish to express their thanks to the Chairman and Members of the Reception and Ladies' Committees ; to the Lord Mayor of Amsterdam, and to the Nederlandsche Yzer en Staalindustrie ; to the chairmen and directors of the works and laboratories in Amsterdam, Ymuiden, Delft, Rotterdam, and Utrecht who kindly invited Members and Ladies to visit them ; to the N.V. Nederlandsche Spoorwegen ; and to all others who collaborated in organizing the Meeting.

OPENING SESSION

The Opening Session was held in the Grand Hotel Krasnapolsky, Amsterdam, on the afternoon of Thursday, 1st October. Mr. A. H. Ingen Housz welcomed the Members and Ladies on behalf of the iron and steel industry of the Netherlands, and the President replied.

Mr. Ingen Housz then gave a short review of the development and organization of the iron and steel industry in the Netherlands, referring to a number of problems concerning technical progress and personnel in the industry. This was followed by a short lecture by Ir. G. W. van Stein Callenfels (Royal Netherlands Blast-Furnaces and Steelworks, Ltd.) on the progress of the Flame Radiation Research being carried out at Ymuiden and elsewhere under the sponsorship of the International Flame Radiation Committee.

A film was then shown, entitled " The Great Jib ", which was a description of the construction of the welded tubular jib of the W.1400 walking dragline of Stewarts and Lloyds, Ltd., Corby.

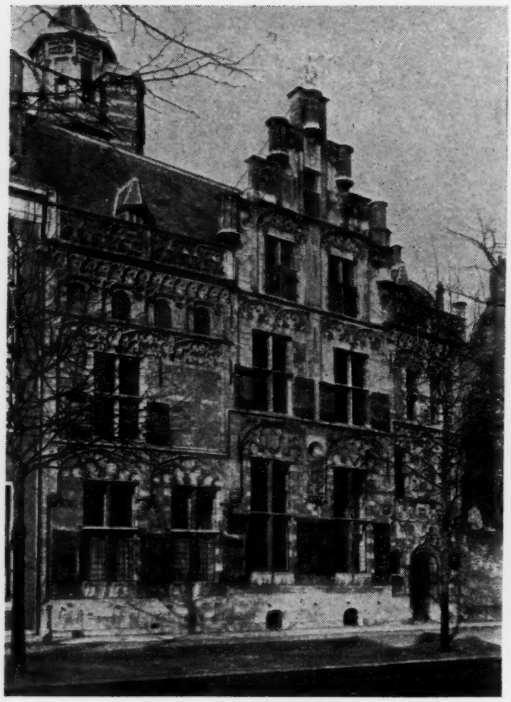
VISITS AND EXCURSIONS

About 300 Members and Ladies attended the Meeting, most of whom arrived in Amsterdam on the evening of 30th September.

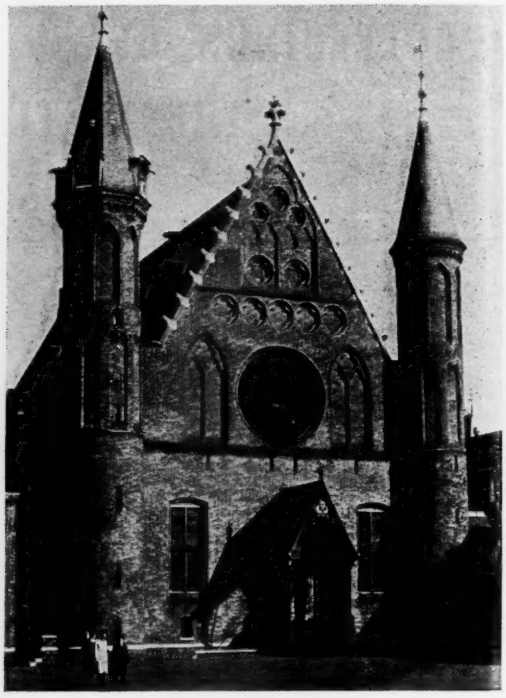
Thursday, 1st October (Amsterdam)

During the morning Members were able to visit either the engineering shops of Werkspoor, N.V., the repair

*The names of those who served on the Reception Committee and a short description of each of the works visited were given in a Detailed Programme Book issued to each Member taking part in the Meeting.



Gemeenlandshuis, Delft



Riddersaal, The Hague

yards and workshops of Amsterdamsche Droogdok Maatschappij, or the shipyards of Nederlandsche Doken Scheepsbouwmaatschappij ; the Ladies and some of the Members visited the works of Asscher's Diamond Industry.

In the afternoon the Opening Session was held at the Grand Hotel Krasnapolsky, and in the evening a reception and buffet were given at the Stedelijk Museum by the Lord Mayor of Amsterdam.

Friday, 2nd October (Ymuiden)

Members spent the whole day visiting the iron and steelworks and the rolling mills of the Royal Netherlands Blast-Furnaces and Steelworks, Ltd., at Ymuiden, with lunch and tea at the works. The Ladies visited Alkmaar cheese market, with lunch at Alkmaar, and had tea at the works at Ymuiden. Much interest was aroused by an exhibition of Van Gogh pictures in the works canteen.

In the evening Members and Ladies attended a supper and dance at the Grand Hotel Krasnapolsky, Amsterdam, at the invitation of the Nederlandsche Yzer en Staalindustrie.

Saturday, 3rd October (Utrecht and Arnhem)

Members visited the steelworks, foundries and rolling mills, etc., of Koninklijke Nederlandsche Staalfabrieken v/h J. M. de Muinck Keizer, near Utrecht, and had lunch in Utrecht. The Ladies visited the Church and the military cemetery at Arnhem and the Hoge Veluwe National Park. They were the guests of the de Muinck Keizer works for the visit and for lunch in the National Park. Members and Ladies had tea at Laren.

Sunday, 4th October (Amsterdam)

Members and Ladies had the morning free and many of them toured the canals and harbours of Amsterdam in water buses ; in the afternoon there was an excursion to Volendam and Marken.

Monday, 5th October (Delft)

Members visited either the National Testing Institute or some of the laboratories of the University of Delft. The Ladies visited the flower market at Aalsmeer and joined the Members for sightseeing and lunch in Delft. Members and Ladies then spent a short time seeing the Binnenhof and the Mauritshuis in the Hague, and had tea at Lisse.

In the evening there was a supper and dance at the Carlton Hotel, Amsterdam.

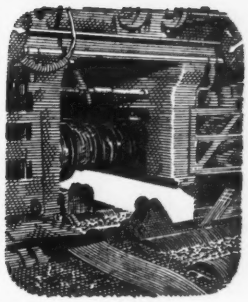
Tuesday, 6th October (Rotterdam)

Members and Ladies were the guests throughout the day of the Nederlandsche Kabelfabriek and the Rotterdamsche Droogdok Maatschappij. They travelled by train to Rotterdam, and had lunch on board a river steamboat while visiting the harbour and docks at Rotterdam and proceeding up river to Alblasserdam. Members then visited either the steelworks and rolling mills of the Nederlandsche Kabelfabriek at Alblasserdam, or the shipbuilding and repair yards and workshops of the Rotterdamsche Droogdok Maatschappij. The Ladies visited Schoonhoven and Gouda by motor-bus.

In the evening Members and Ladies had dinner at the Atlanta Hotel, Rotterdam, thus concluding the Meeting.

All those who took part were greatly impressed by what they saw in the various works, and much enjoyed the opportunity of seeing the Dutch countryside, its fine buildings, both old and new, and the many magnificent works of art. They will also remember with gratitude the unfailing kindness and overwhelming hospitality shown to them by their Dutch hosts.

[*The three photographs are reproduced by permission of the Netherlands National Tourist Office.*]



Roll Pass Design For Beams

By D. A. Winton, B.Sc. (Eng.), A.M.I.C.E., A.M.I.Mech.E.

SYNOPSIS

Roll-pass design is discussed, with particular reference to several pass schedules in present use in rolling mills, for the square and diagonal methods of rolling beams to conform with British Standards Institution Specification No. 4 (1932). The basic principles of roll-pass design, the influence of the design of the mill on the roll design, roll clearance, and the position of the passes relative to the pitch line are discussed.

The areas of the passes of the schedules examined are given, and curves are suggested from which the number of passes and the areas of the billet and of each pass can be obtained for a schedule to roll any size of beam. The desirability of ensuring that the percentage reduction in area is uniform over the pass is stressed.

Details of the mills and rolls used in the various schedules referred to are given in an Appendix. 821

In engineering constructional work, 'beams' may have various shapes of cross-section. In rolling, however, it is usually assumed that this term refers to the shape shown diagrammatically in Fig. 1*a*; it is also often called a joist. This report deals with the roll pass design for such sections, which are usually rolled to conform with British Standards Institution Specification No. 4 (1932). As in that specification, this shape of section will be referred to as a beam.

The flanges of a beam are both of the same width, designated dimension B in B.S.4, and their outside surfaces are at an angle of 90° to the web. They decrease in thickness from the root to the toe, which is rounded. The length of the web, dimension A, is usually greater than the width of the flanges, and the difference between dimensions A and B increases with size of the beam.

Beams are also rolled in which the flange widths are either equal to or a substantial fraction of the web length, particularly for the larger sections, and are known as 'broad flange beams.' They have parallel flanges and their toes are square. Details of such beams, a cross-section of which is shown in Fig. 1*b*, are not included in this report.

The number of stands or sets of rolls required to reduce a billet to a beam section depends on the number of passes that can be accommodated in the roll lengths. Usually, two or three stands are used. If three stands are necessary the rolls are termed roughing, intermediate or forming, and finishing rolls, respectively; if two are used they are termed roughing and finishing rolls. The last pass of a schedule is often referred to as the finishing pass. Passes are placed so that the web is either horizontal or inclined at a comparatively small angle to the horizontal.

The radii of the root and the toes of the flanges are also specified in B.S.4. The radii decrease in succeeding passes of a schedule until those of the finishing pass will give the correct shape to the stock.

In some schedules the last two passes are identical, the additional pass being cut as an economy measure to lengthen the roll life. When the dimensions of the stock leaving the finishing pass are the maximum tolerated by any particular specification, the rolls must be removed from the mill and machined to reduce the dimensions of the pass to their original size. This process is usually referred to as 'dressing.' A second finishing pass will thus increase both the time between dressings and also the roll life, assuming that the wear in the leader pass (the penultimate pass) has not been such as to necessitate an excessively large reduction in the finishing pass.

BASIC PRINCIPLES

Before dealing with the various methods of rolling a beam, those principles of roll design common to all methods and which must be followed in designing the rolls for a beam will be mentioned briefly.

(i) If stock is rolled in a groove which has straight parallel sides normal to the axes of the rolls, it can be reduced only in the vertical direction (with horizontal rolls), for the stock could not enter the rolls if its horizontal dimensions were greater than those of the groove (*see* Fig. 2*a*).

When stock is rolled between horizontal roll surfaces, it is said to be subject to 'direct compression' or 'slabbing action' (Fig. 2*b*); if the surfaces of the rolls compressing the stock are very nearly normal to the axes of the rolls, the stock is

Paper MW/AA/14/52 of the Roll Design Conference of the Mechanical Working Division of the British Iron and Steel Research Association, first received 18th November, 1952, and in its final form on 31st July, 1953. The views expressed are the author's, and are not necessarily endorsed by the Conference as a body.

Mr. Winton, formerly Technical Secretary of the Mechanical Working Division of the Association, is now with the British Iron and Steel Federation.

Table I

AREA PER PASS, sq. in., AND PERCENTAGE REDUCTION PER PASS

Schedule	Dimensions of Beam, in. × in.	Weight, lb./ft.	Cross-Sectional Area When Cold, sq. in.	Pass Number															
				Billet	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
A	3 × 1¼	4·0	1·18	7·3	5·1	3·9	3·2	2·4	1·8	1·4	1·2									
				30·0%	22·7	19·0	23·5	25·5	21·2	13·5										
B	3 × 3	8·5	2·52	13·0	11·1	9·0	7·1	5·4	4·4	3·3	2·8	2·6								
				14·2%	19·5	21·5	23·5	20·5	22·5	14·5	8·5									
C	3¼ × 3*	9·7	...	17·2	13·7	9·4	7·2	5·6	4·3	3·5	2·9									
				20·3%	31·0	23·2	23·5	23·3	18·7	15·8										
D	4¼ × 4¼*	18·0	...	27·3	25·0	21·3	18·2	14·3	11·3	8·8	7·5									
				8·5%	15·0	15·0	21·5	21·0	22·0	15·0	14·0	6·5	5·7							
E	5 × 4¼†	18·0 (20)	...(5·88)	30·5	29·1	25·0	21·0	17·3	13·6	10·1	9·0	7·5	6·0	5·2						
				5·0%	14·0	16·0	17·6	21·5	26·0	9·5	17·0	20·0	5·0							
F	5 × 4¾†	18·0 (20)	...(5·88)	46·8	42·4	33·8	26·1	22·7	17·9	14·4	11·8	10·6	9·0	7·4	5·9	5·6				
				9·5%	20·5	23·0	13·0	21·0	20·0	17·8	11·0	15·2	18·0	19·5	5·5					
G	5 × 4¾†	18·0 (20)	...(5·88)	31·0	25·3	22·3	18·4	13·2	10·4	8·6	7·1	6·2	5·9	5·4						
				18·2%	11·5	17·5	18·2	20·5	17·2	17·5	13·0	4·5	8·5							
H	6 × 3	12·0	3·53	32·0	28·9	23·7	18·5	14·5	10·9	8·0	6·3	4·9	3·9	3·6						
				10·0%	18·0	22·0	21·8	25·0	26·5	21·5	22·5									
I	6 × 5	25·0	7·37	35·0	35·0	29·7	23·5	17·7	13·8	11·1	9·3	8·2	7·5	7·6	3·0	7·4				
				0%	15·0	21·0	25·0	22·3	19·5	15·8	12·2									
J	8 × 4†	19·3 (18)	...(5·30)	44·0	34·7	23·4	17·5	13·5	10·0	7·5	6·4	5·5								
				21·2%	32·5	25·5	23·0	26·0	25·0	15·0	14·0									
K	8 × 5	28·0	8·28	61·3	58·1	43·8	32·9	20·6	15·3	12·6	11·1	9·6	8·3	8·2						
				4·5%	24·5	24·5	37·3	25·5	17·8	11·8	13·3	13·5	1·5							
L	8 × 6	35·0	10·30	63·4	58·1	44·6	35·6	23·8	18·3	16·0	13·4	11·9	10·9	10·1						
				8·2%	22·2	20·6	33·0	23·2	12·7	16·0	11·5	7·5	7·5							
M	9 × 7	50·0	14·71	76·0	74·5	55·6	43·5	29·9	24·5	21·0	18·5	16·6	15·5	14·4						
				2·0%	25·5	21·5	31·0	19·5	14·5	12·0	10·0	6·5	7·2							
N	10 × 6	40·0	11·77	...	49·6	39·6	30·4	24·5	19·8	16·6	15·0	12·8	12·1							
				...	20·0%	23·0	19·0	19·0	16·0	10·0	15·0	5·0								
O	12 × 5	32·0	9·45	100·0	100·0	75·2	59·2	44·7	35·7	25·5	20·0	16·4	12·4	10·4	9·5					
				0%	24·8	21·5	24·8	20·0	28·5	21·5	18·0	24·5	16·5	8·7						
P	12 × 6	44·0	13·00	110·0	110·0	97·7	84·7	71·5	57·9	49·5	39·1	30·8	24·9	18·7	16·3	14·2				
				0%	11·5	13·3	15·5	19·0	14·2	20·5	21·0	19·5	24·8	12·5	12·8	0·5				
Q	12 × 6	54·0	15·89	127·5	127·5	108·7	90·7	73·0	68·2	61·6	56·8	44·5	34·4	28·0	21·5	21·1	19·5	17·9	16·3	
				0%	15·0	16·5	19·6	6·8	10·0	8·0	21·5	23·0	18·5	23·2	1·5	7·8	8·5	9·0		
R	12 × 8	65·0	19·12	100·0	100·0	92·4	80·3	62·3	50·0	41·6	34·5	29·0	24·5	21·0	19·6					
				0%	7·6	13·0	22·3	20·0	16·8	17·2	16·0	15·6	14·5	6·5						
S	20 × 6½	65·0	19·12	220·0	220·0	192·0	177·0	132·0	117·0	102·0	81·0	73·0	60·0	55·2	50·0	41·0	29·8	25·6	19·5	19·2
				0%	13·0	8·0	25·5	11·5	12·5	20·5	10·0	18·0	8·5	9·5	18·0	27·5	14·0	24·0	2·0	

* Not British Standard Section
† British Standards figures shown in brackets

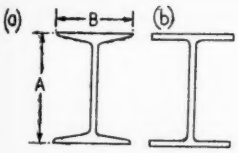


Fig. 1—Cross-section of (*a*) standard beam, (*b*) broad flange beam

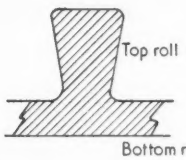


Fig. 3—Pass forming a re-entrant angle in the roll

subjected to ' sidework ' (Fig. 2*d*), and stock rolled between these two extremes is rolled on the ' diagonal ' (Fig. 2*c*). Thus, the web of a beam is subjected to direct compression or slabbing action during rolling, and the flanges are subjected mainly to sidework. From what follows it will be clear that it will be easier to reduce the area of the web than that of a flange.

(ii) It is easier to enter the stock into rolls with inclined surfaces than into those with vertical surfaces, as there is a greater horizontal latitude in the entering position of the stock. Another advantage of rolling between inclined surfaces is that the stock is well gripped by the rolls throughout the arc of contact and, also, is released by the rolls as soon as it has passed beyond the plane containing their axes.

(iii) It is not possible to roll stock through a groove in a pass which forms a re-entrant angle in one of the rolls, as the stock would not leave the rolls (*see* Fig. 3).

(iv) The gaps between the two rolls adjacent to each pass are known as the ' roll joints.' The position of the roll joints relative to the stock is important in regard to the manner in which the stock is reduced. Figure 4 shows the reduction of stock in a groove which occurs when rolling a beam. The roll joints can be at either the toe or some point on the outside of the flanges. Figure 4*a* shows the flanges rolled in grooves each formed by one roll only; the flanges are thus said to be rolled in ' closed ' (dead) grooves. Any reduction in area of a flange is caused by compression in one roll only, and it is easier to reduce the height of the flange than its width.

In Fig. 4*b* the top flange is rolled in a groove formed by both rolls, *i.e.*, an ' open ' (live) groove. The bottom flange is rolled in a closed groove. In the open groove the two sides of the groove approach each other over the arc of contact, the flange is subjected to sidework, and its thickness can be reduced. The two sides, however, move at different peripheral speeds and cause rubbing between the stock and the rolls, in addition to the speed differences in each roll from the bottom to the top of the groove (this also occurs in a closed groove). The height (diameter) of the collar must be such that it will prevent the stock being bent over into the roll gap as in Fig. 4*c*. If this occurs the stock will get jammed in the rolls or the toe of the flange may be sheared off.

From the above it is clear that, in general, it is easier to reduce the height (width) of the flange in a closed than in an open groove, and to reduce its thickness in an open groove. When rolling beams, therefore, the rolls are usually designed so that the positions of the roll joints relative to the stock are changed at each successive pass. This is not always possible with some sections, owing to their shapes.

Figures 4*a–c* have been drawn to exaggerated scales, to illustrate more clearly the various points discussed. The ratio of the height of the stock to the diameter of the rolls is much greater than that used in practice.

METHODS OF ROLLING

A beam is usually rolled by either the ' square ' or the ' diagonal ' method; typical pass shapes used in these methods are sketched in Figs. 5*a* and *b*. Pass shapes used in actual rolling schedules in several works in this country are shown in Figs. 6*a–r*. These representative schedules have been selected from a more complete set provided by members of the B.I.S.R.A. Roll Design Conference and covering the range of sections rolled by them. Most of the schedules are used for rolling sections that conform to B.S.4, and it is understood that all of them are in present use except those for 3 in. × 3 in. and 8 in. × 4 in. beams. Frequent reference to these designs will be made in the following discussion of roll pass design. Details of the pass areas and the mills in which these schedules are rolled are given in Tables I and II. For convenience, the works are numbered from I to VIII and the schedules are lettered *A* to *S*.

The square method of rolling is used in all but two of the schedules examined. These two exceptions, the schedules for the 3 in. × 1½ in. beam *A* and the 3¼ in. × 3 in. beam *C*, use the diagonal method.

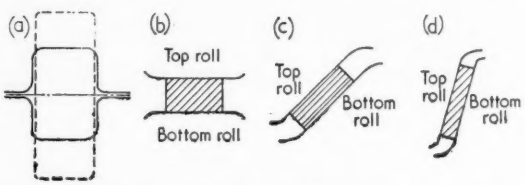


Fig. 2—Designs for rolling: (*a*) Vertical pass; (*b*) direct compression or slabbing action; (*c*) diagonal rolling; (*d*) sidework

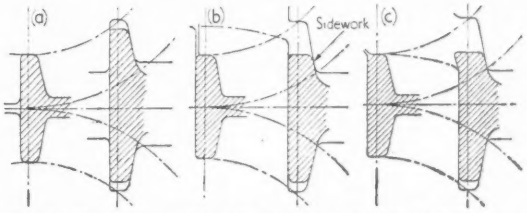


Fig. 4—Vertical sections in grooves of rolls: (*a*) Flanges rolled in a closed groove; (*b*) flanges rolled in an open groove; (*c*) showing stock bent over into roll gap

Table II
DETAILS OF MILLS AND ROLLS

Works	Dimensions of Section, in. × in.	Schedule	Mill: Type	Mill: Nominal Roll Diameter, in.	Mill: Motive Power	Mill: Rate of Production, tons/hr.	Mill: Descaling	Rolls: Quality	Rolls: Length L ft. in.	Rolls: Diameter D ft. in.	Rolls: L/D	Rolls: Reduction in Diameter at Each Dressing, in.	Rolls: Amount Rolled Between Dressings, tons	Rolls: Total Reduction in Diameter, in.	Rolls: Total Amount Rolled, tons	Rolls: Width of Finishing Pass at Discard in.
I	4½ × 4½	D	3 stands, 2-high reversing	24	Steam	20	Compressed air	Roughing: Steel or grain cast iron	6 0	2 2	2·77	⅜	2500	2½	17,000	4⅝ D
	5 × 4½	E														5⅛ E
	6 × 5	I						Finishing: Grain cast iron	4 10½	2 2⅜	2·22	⅜	1000	2⅜	7500	6 7/16 I
II	3 × 3	B	2 stands, 3-high	17	Steam	12	Steam	Grain cast iron	4 3	1 5	3·0	¼–½	95	2	Not known	3 5/16 B
	8 × 4	J	2 stands, 2-high reversing	32	Steam and electric	20	Steam	Grain cast iron	6 6	2 8	2·43	¼–½	250	4½	3000	8 7/16 J
III	5 × 4½	F	2 stands, 2-high reversing	36	Electric	30	Steam and compressed air	Alloy cast steel	7 2⅜	3 0	2·40	½	1500	5	15,000	5 1/16 F
	12 × 6	Q				44		Grain cast iron	7 2⅜	3 0	2·40	½	1000	4	8000	12¼ Q
	20 × 6½	S				35		Forged steel	7 2⅜	3 0	2·40	⅜	1000	5	13,000	20 7/16 S
IV	3 × 1½	A	Roughing: 2 stands, 3-high; Finishing: 2-high reversing	14⅜ 14½	Electric	20	Water	Roughing: Alloy cast steel	3 3⅜	1 2⅜	2·69	⅛	300	1½	4500–8000	3 3/4 A
								Finishing: Alloy cast steel	3 3⅜	1 2⅜	2·67	⅛	300	1½	4000	
	12 × 6	P	2 stands, 2-high reversing	35	Electric	65	Steam	Roughing: Cast steel	7 9	2 11	2·66	1	8000	5	40,000	12¼ P
								Finishing: Cast steel	6 6	2 11	2·23	½	1000	5	10,000	
V	5 × 4½	G	2-high reversing	27	Steam	30	Steam	Roughing: Carbon steel	5 10 7/16	2 4	2·52	3/16	800	2⅜	8000	5 1/16 G
								Finishing: Alloy steel	5 6½	2 4	2·38	1/16				
	8 × 5	K	3 stands, 2-high reversing	36	Steam	35 to 40	Steam	Roughing: Alloy steel	8 3½	3 2½	2·60	3/16	1800	2½	60,000	8 1/16 K
	8 × 6	L						Intermediate: Alloy steel; Finishing: Carbon steel	6 9½	3 2¼	2·15	3/16	1800	2¼	20,000	8 1/16 L
	9 × 7	M	3 stands, 2-high reversing	36	Steam	40	Steam	Roughing: Carbon steel	8 3½	3 2	2·62	3/16	4500	3	30,000	9 1/16 M
								Intermediate: Special grain cast iron								
								Finishing: Special grain cast iron	6 9½	3 2	2·15	3/16				
VI	3¼ × 3	C	2 stands, 2-high reversing	16	Electric	8	Water	Alloy steel	4 0	1 6	2·67	1/16	500	3¼	5000 (estimated)	3 C
VII	6 × 3	H	2 stands, 2-high reversing	32	Information not available			Information not available	6 0	2 8	2·11	Information not available				H
	12 × 5	O	3 stands, 2-high reversing	32	Information not available			Information not available	6 0	2 8	2·11					O
	12 × 8	R	3 stands, 2-high reversing	32½ and 33	Information not available			Roughing	6 0 3/16	2 8½	2·23					R
								Intermediate	6 0 3/16	2 9	2·19					
								Finishing	5 10 11/16	2 9	2·14					
VIII	10 × 6	N	2 stands, 2-high reversing	34	Information not available			Roughing	7 9	2 10	2·73	Information not available				N
								Finishing	6 6	2 10	2·30					

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Square Rolling

In square rolling, the billet enters the first pass with its long side vertical; the billet must be narrower than the pass so that it can enter the rolls. In subsequent passes the width of the stock is increased and its height is decreased. The flanges are formed early in the roughing passes and have a pronounced taper to facilitate the reduction of the stock. The taper is made less in each pass until the flanges in the finishing pass have the taper required by the specification.

Diagonal Rolling

In diagonal rolling, the flanges can be reduced in thickness more easily than in square rolling, where sidework only can be applied. The extent to which the section can be rolled on the diagonal, *i.e.*, the inclination of the web to the horizontal, depends on the flange taper. The angle between the web and the horizontal decreases throughout a schedule from as much as 15° in the first pass to about 5° in the finishing pass, the stock being tilted to the appropriate angle when entering a pass. The maximum angle occurs when one of the tapered surfaces is vertical, but this angle can be increased as in schedule *C* by distorting the section.

Another advantage of diagonal rolling is that, when machining the rolls to regain the original dimensions of the pass, less needs to be cut off from them than when square rolling is used. One of the grooves in each roll is, however, deeper than either of those in square rolling, as will be seen from Fig. 5, especially for beams with wide flanges or long webs.

The wear of the rolls and the delivery guides is usually less in diagonal rolling, for, as mentioned previously, the rolls and the stock are not in contact beyond the plane containing the axes of the rolls, which thus do not grip the stock at exit. For this reason, therefore, the backs of the flanges of schedules based on the square method of rolling are often tapered by about 1° or 2°. In the finishing pass there may be a taper of about ¼°.

The greater ease with which stock can be reduced in diagonal rolling suggests that fewer passes might be required for this method than in square rolling. However, as only two schedules based on diagonal rolling were available it is difficult to determine whether this conclusion is borne out in practice, particularly as schedules not rolled in the same mill are compared; it appears from Table I that the diagonal method may give a quicker reduction, as the roughing passes of schedules *A* and *C* have a greater percentage reduction in area than those of a comparable size rolled on the square.

A disadvantage of the diagonal method when rolling beams of varying web thickness by lifting the rolls, but with all other dimensions unchanged, is that both the flange thickness and width are increased. For square rolling, only the flange width is increased.

Slick Rolling

It is understood that this method (Fig. 5*c*), in which the web is bent up and down alternately in succeeding passes, is used in the U.S.A. The flanges can be subjected to diagonal rolling, but presumably without giving rise to end thrust (*see* below). However, as it is believed that this method is seldom used in this country and none of the schedules used it, no further consideration is given to it in this report.

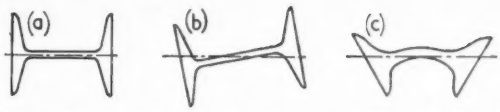

Fig. 5—Passes for various rolling methods: (*a*) Square rolling; (*b*) diagonal rolling; (*c*) slick rolling

TYPES OF PASS

The roll force arising from the reduction in area of the stock may exert an end thrust on the rolls which it is desirable to reduce to a minimum, or preferably to eliminate, as it causes increased wear of the inclined and vertical surfaces of the rolls and ultimately gives a distorted section as the rolls become displaced one to another.

The passes illustrated in Figs. 7*a* and *b* practically eliminate end thrust on the rolls in square rolling. The pass in Fig. 7*b* is mostly used; the roll joints are shown in the bottom half of the pass, but they could, of course, be in the top half. The pass in Fig. 7*a* cannot be used throughout a schedule, as the roll joints are in the same position relative to the stock throughout, and fins would probably be formed in the middle of the backs of the flanges and would be difficult to remove. Also, the flanges would be reduced only in closed grooves throughout a schedule, and it would thus be difficult to reduce their thickness. This type of pass, however, is convenient to use in the first few roughing passes of a schedule when a large billet is available. The top roll is lifted and several runs are made through one pass, the top roll being lowered for each run, as shown in schedule *S* (Fig. 6*p–r*).

In those schedules rolled on the diagonal, passes with roll joints in positions as shown in Fig. 7*c* are used. With square rolling, the end thrust is usually balanced at all points on the arc of contact. This may not be so with diagonal rolling, and care must be taken that the summation of end thrust over the complete arc of contact is as small as possible. In the particular example shown in Fig. 7*c*, the top half of the right-hand flange and the bottom half of the left-hand flange are enclosed by the top and bottom rolls, respectively, at all points on the arc of contact and should therefore exert only little end thrust. However, the top half of the left-hand flange and the bottom half of the right-hand flange are reduced by both rolls, and this will cause some end thrust. The reduction of the web offsets this to some extent.

Collars are provided to take up any end thrust that does occur; their thrust surfaces are often inclined at a small angle of 1° or 2° to reduce the friction between the rolls. The collars may be between passes in the middle of the rolls, or at their ends.

ROLL JOINTS

If the stock is rolled on the square in a 2-high mill and each successive closed pass has the roll grooving as in Fig. 8*a*, it will be difficult to control accurately the dimensions of the section, as the same halves of the flanges will be rolled continuously in either the

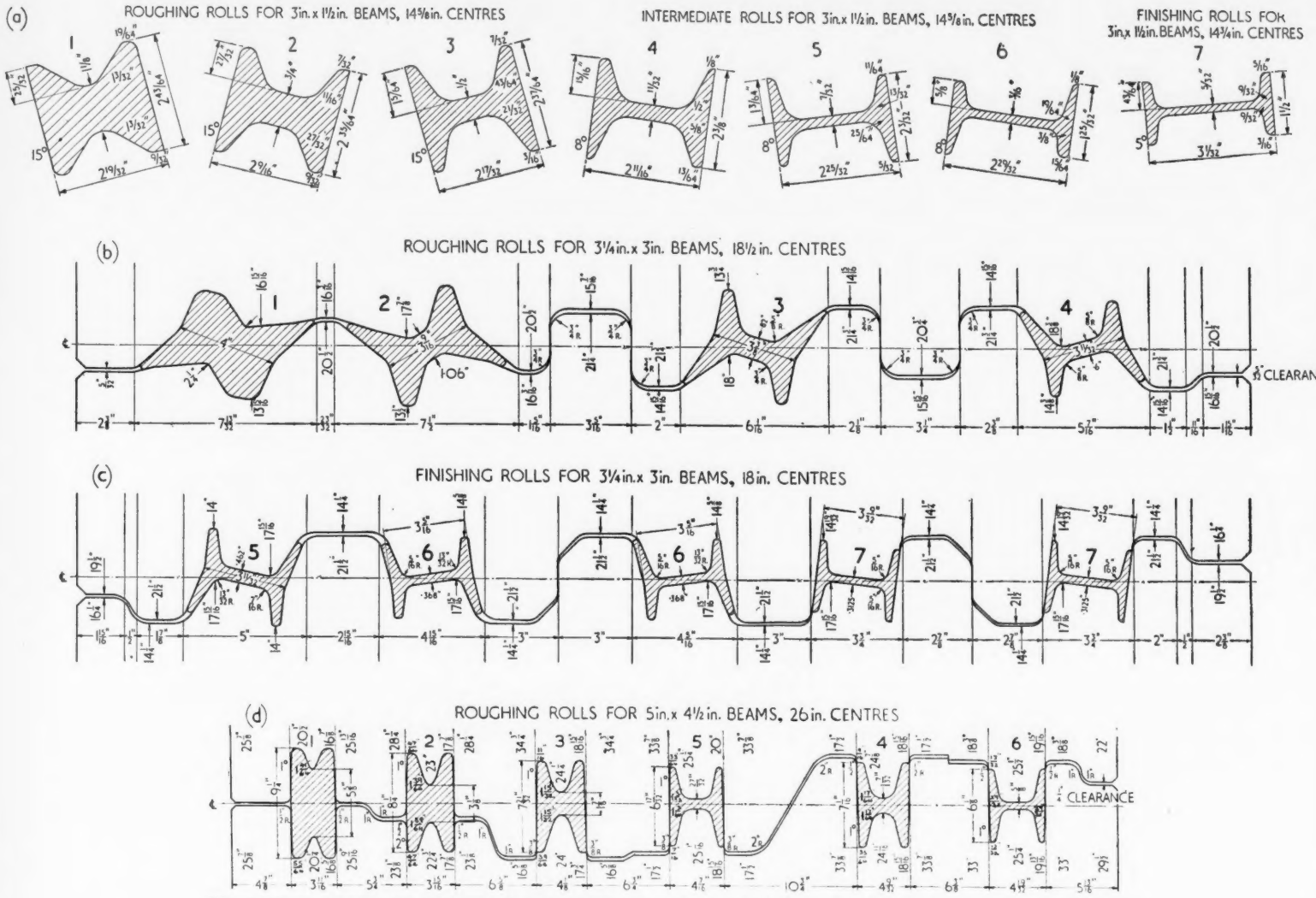
(a)
ROUGHING ROLLS FOR 3in. x 1½in. BEAMS, 14⅝in. CENTRES
INTERMEDIATE ROLLS FOR 3in. x 1½in. BEAMS, 14⅝in. CENTRES
FINISHING ROLLS FOR 3in. x 1½in. BEAMS, 14¾in. CENTRES
(b)
ROUGHING ROLLS FOR 3¼in. x 3in. BEAMS, 18½in. CENTRES
CLEARANCE
(c)
FINISHING ROLLS FOR 3¼in. x 3in. BEAMS, 18in. CENTRES
(d)
ROUGHING ROLLS FOR 5in. x 4½in. BEAMS, 26in. CENTRES
CLEARANCE

Fig. 6—Pass shapes: (*a*) Schedule *A*, Works IV; (*b*) and (*c*) schedule *C*, Works VI; (*d*) schedule *E*, Works I

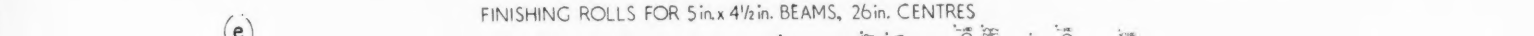

Fig. 6—Pass shapes: (*a*) Schedule *A*, Works IV; (*b*) and (*c*) schedule *C*, Works VI; (*d*) schedule *E*, Works I

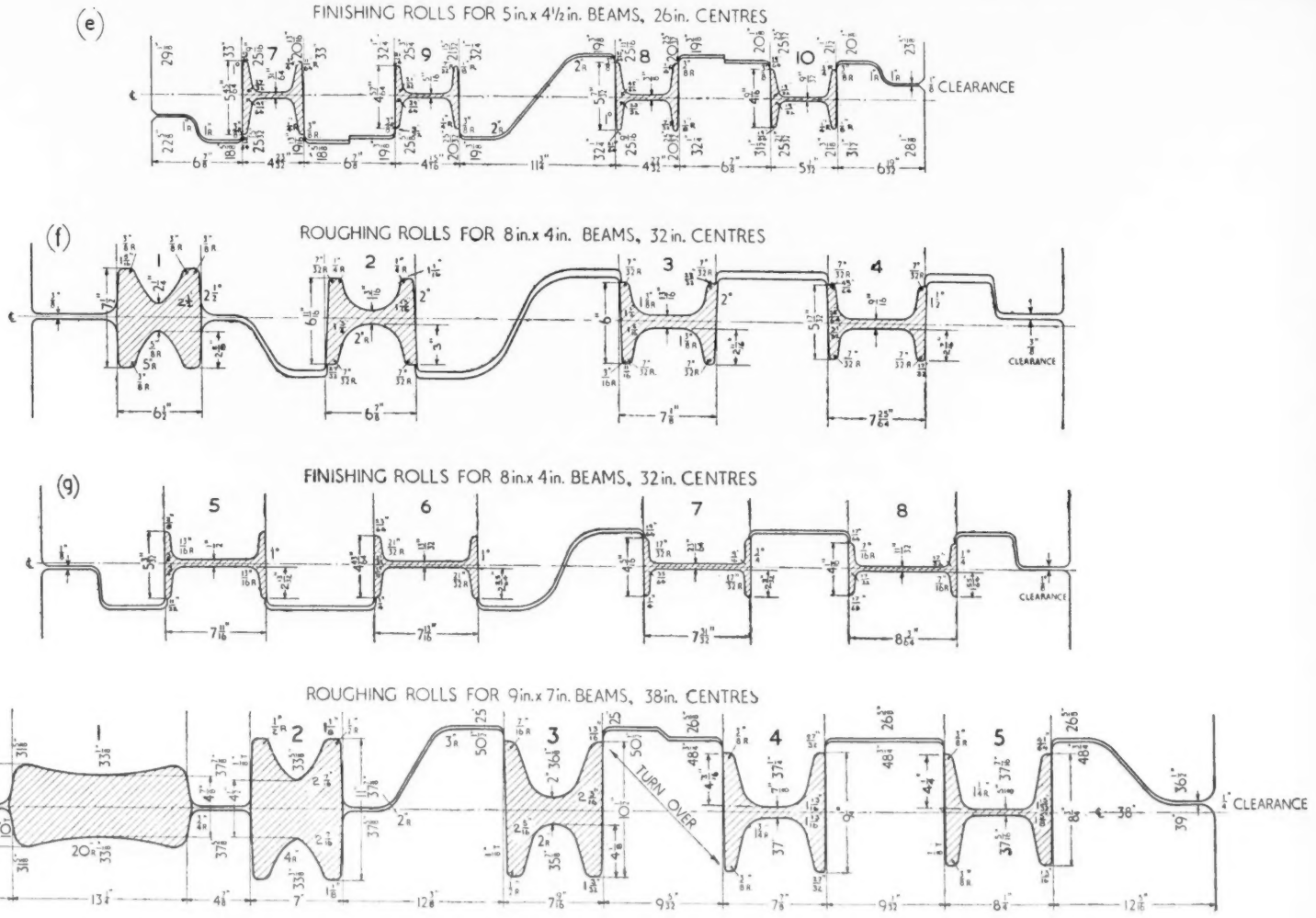
(e)
FINISHING ROLLS FOR 5 in. x 4½ in. BEAMS, 26 in. CENTRES
CLEARANCE
(f)
ROUGHING ROLLS FOR 8 in. x 4 in. BEAMS, 32 in. CENTRES
CLEARANCE
(g)
FINISHING ROLLS FOR 8 in. x 4 in. BEAMS, 32 in. CENTRES
CLEARANCE
(h)
ROUGHING ROLLS FOR 9 in. x 7 in. BEAMS, 38 in. CENTRES
TURN OVER
CLEARANCE

Fig. 6 (cont.)—Pass shapes: (*e*) Schedule *E*, Works I; (*f*) and (*g*) schedule *J*, Works II; (*h*) schedule *M*, Works V

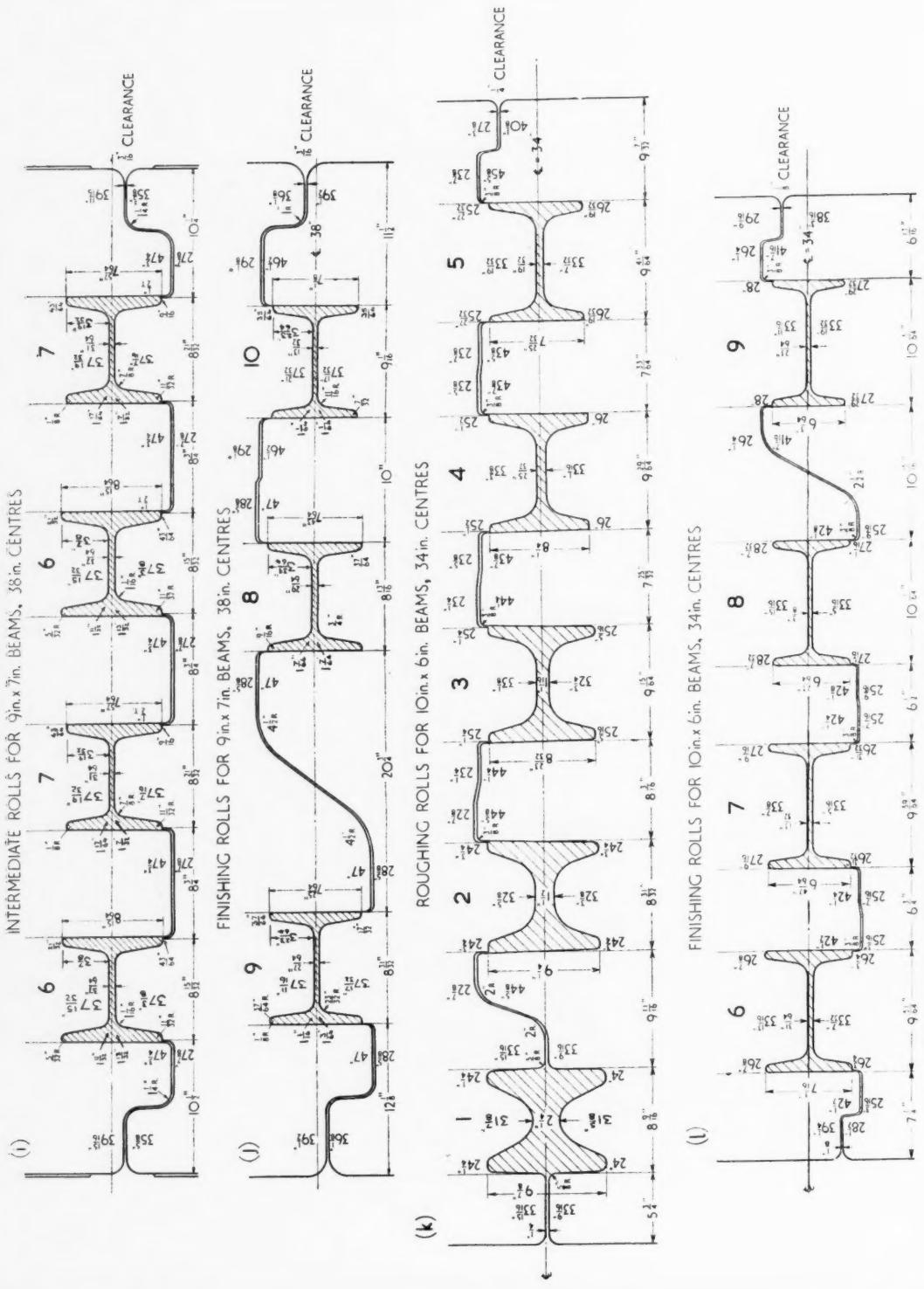

Fig. 6 (cont.)—Pass shapes: (*i*) and (*j*) Schedule *M*, Works V; (*k*) and (*l*) schedule *N*, Works VIII

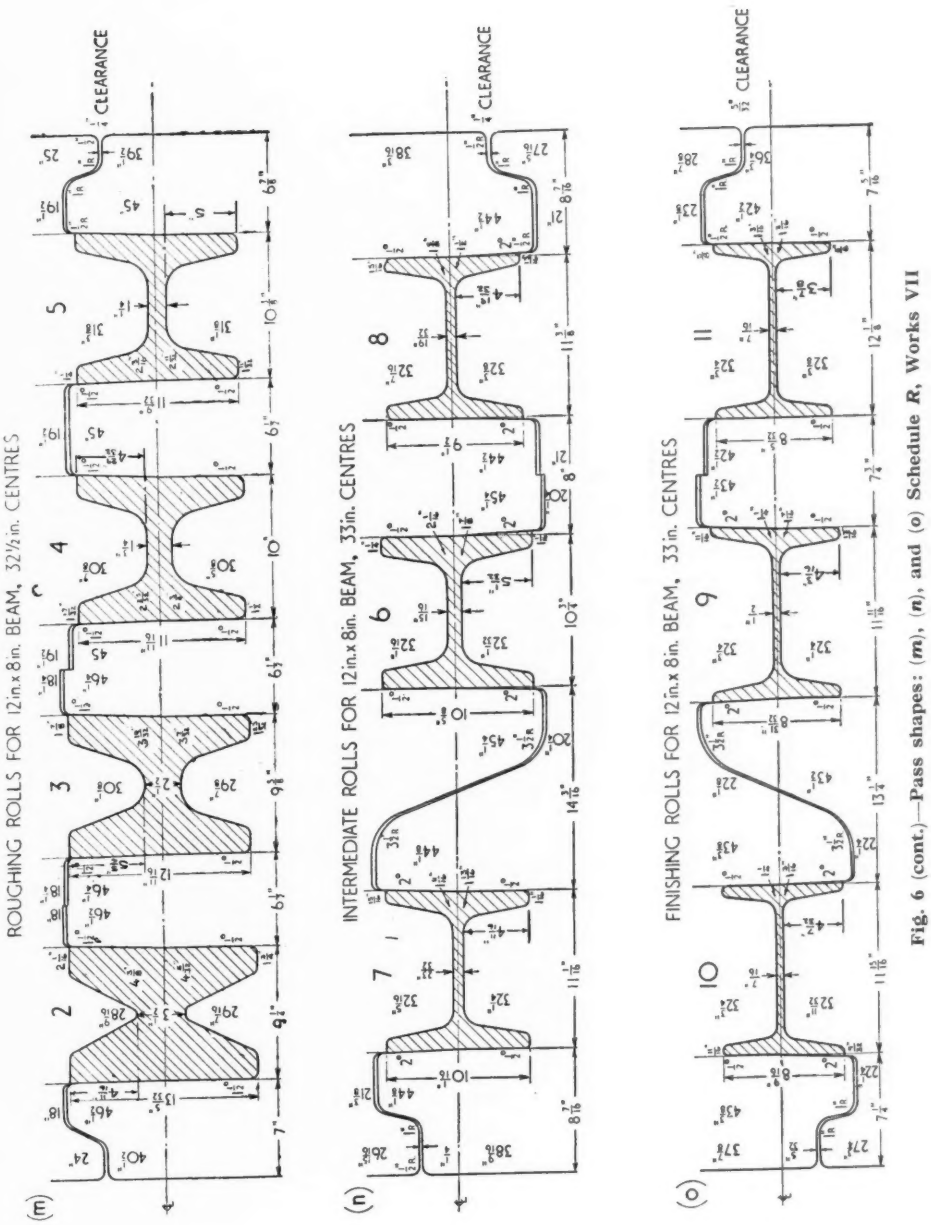
ROUGHING ROLLS FOR 12in.x 8in. BEAM, 32½in. CENTRES
INTERMEDIATE ROLLS FOR 12in.x 8in. BEAM, 33in. CENTRES
FINISHING ROLLS FOR 12in.x 8in. BEAM, 33in. CENTRES
CLEARANCE
(m)
(n)
(o)

Fig. 6 (cont.)—Pass shapes: (*m*), (*n*), and (*o*) Schedule *R*, Works VII

Fig. 6 (cont.)—Pass shapes: (*i*) and (*j*) Schedule *M*, Works *V*; (*k*) and (*l*) schedule *N*, Works VIII

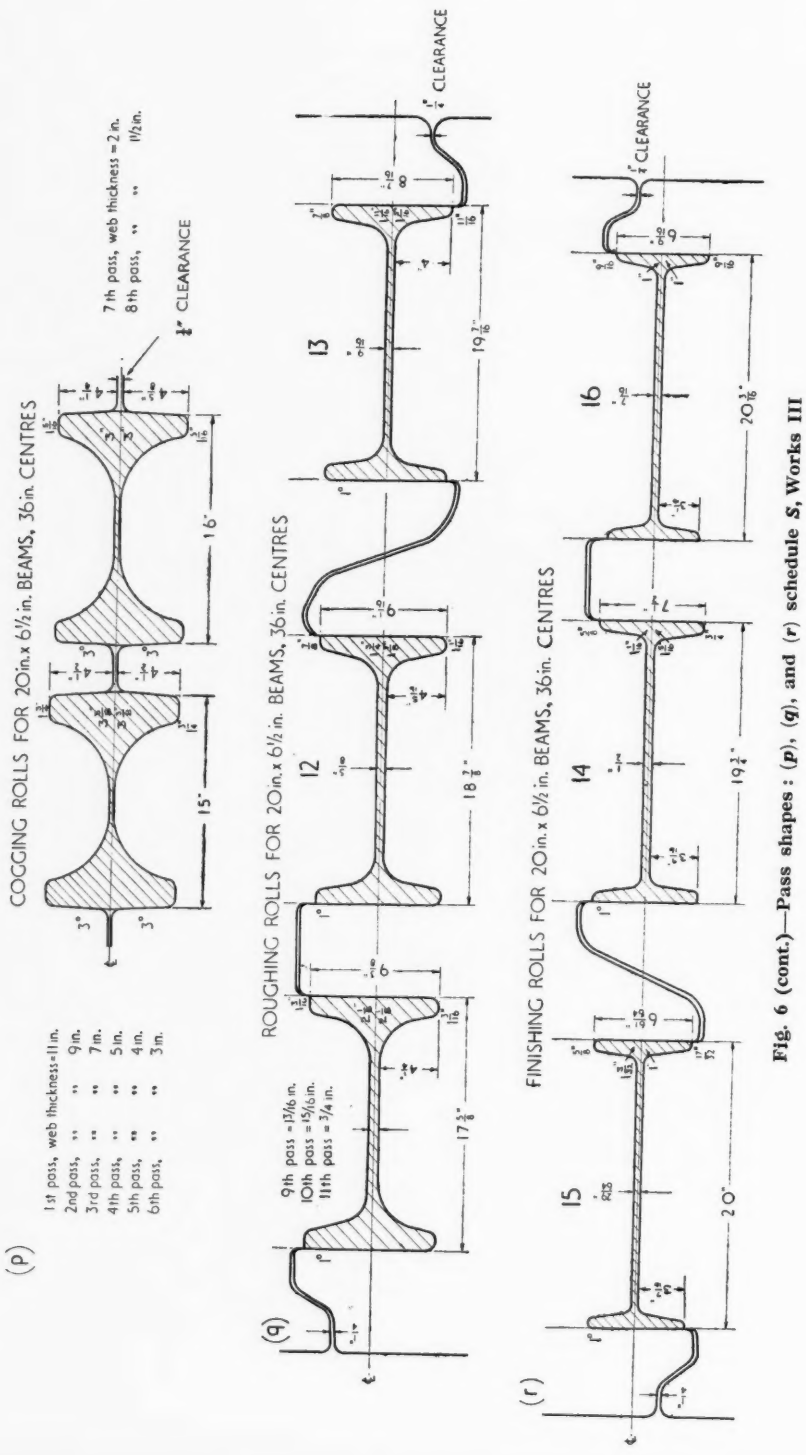

Fig. 6 (cont.)—Pass shapes : (p), (q), and (r) schedule S, Works III

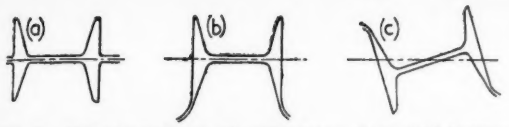

Fig. 7—Usual positions of roll joints: (*a*) and (*b*) Square rolling; (*c*) diagonal rolling

closed or the open parts of the pass (*see* p. 5). In addition, fins may be formed at the toes of the flanges adjacent to the roll joints after the stock has been rolled through several passes. These difficulties can be overcome in several ways. One method, if turning gear is available, is to turn stock through 180° between each pass. Another method is to use cross-collars as shown in Fig. 8*b*; this, however, requires a greater length of roll and the number of passes per roll will be reduced. Figure 8*c* shows how the number of cross-collars can be reduced by placing consecutive passes so that they are not adjacent to each other. In the example shown only one cross-collar is required, compared with three for that shown in Fig. 8*b*. Thus, only one cross-collar is necessary if it is placed in the middle of the rolls, but the time of travel between passes is increased.

The use of alternate passes between, say, the bottom and middle rolls and the middle and top rolls in a 3-high mill makes it unnecessary either to turn the stock through 180° or to cross-collar (*see* Fig. 9).

If the diagonal method of rolling is used, the flanges can be rolled alternately in open and closed grooves both in 2-high and in 3-high mills by changing the direction of tilt in consecutive passes (*see* Fig. 10).

The passes should be numbered so that the last pass in the set of rolls delivers the stock as near as possible to the exit from the stand. If for any reason the number of passes has to be altered, it should be either increased or decreased by an even number, so that the side of delivery from the mill is unchanged.

ROLL CLEARANCE

Roll clearance, which is often called roll spring, is the distance apart, in the plane containing the axes of the rolls, of those horizontal surfaces at the roll ends which do not form the passes, when stock is passing through the rolls.

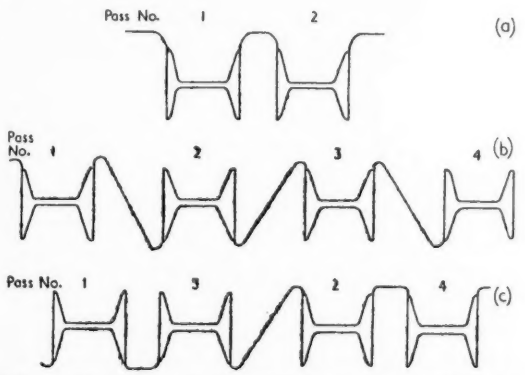

Fig. 8—Types of roll grooving for square rolling in a 2-high mill

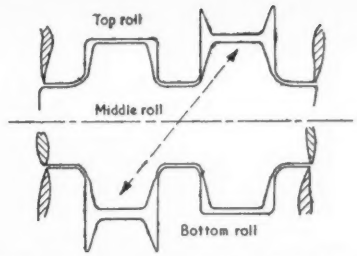

Fig. 9—Roll grooving for square rolling in a 3-high mill

When stock enters the rolls they spring apart as a result of the roll force arising from the reduction of the stock. The stretch in the mill housing and any slack in the bearings, chocks, etc., all contribute to the spring, which thus gives a clearance between the rolls during rolling. Apart from this, clearance must be allowed for to offset the effects of roll wear in the passes, particularly wear of their horizontal surfaces. When wear takes place the rolls can be brought closer together, thereby ensuring that the rolled stock continues to have the required dimensions. The clearance decided upon must be greater than the spring due to the reduction of the stock, so that the rolls can revolve freely when the mill is unloaded, without any tendency for one roll to drive the other. This is particularly important if the rolls do not have the same diameter.

For the schedules examined, the clearances vary from about $\frac{1}{8}$ in. for finishing rolls to about $\frac{1}{4}$ in. for roughing rolls.

PITCH LINE

The pitch line, or centre-line, of the rolls is that line parallel with the axes of the rolls which bisects the distance between them. The circumferential speeds

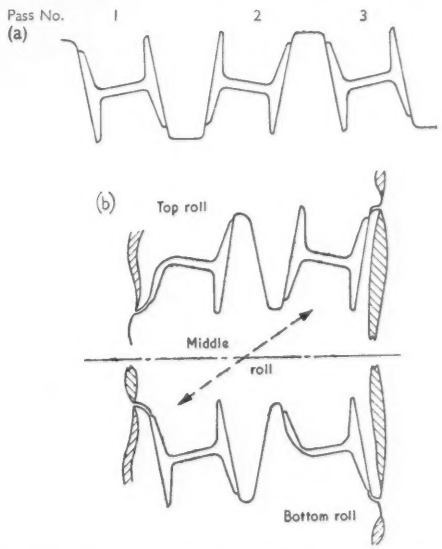

Fig. 10—Roll grooving for diagonal rolling: (*a*) 2-high; (*b*) 3-high

Table III

AVERAGE REDUCTION PER PASS FOR ALL SCHEDULES

Pass Number	Billet	1	2	3	4	5	6	7	8	9	10	
Reduction in area per pass, %		10	20	23	23	22	20	18	15	13	10	etc.
Elongation per pass, %		11·1	25·0	29·9	29·9	28·2	25·0	21·9	17·7	14·9	11·1	etc.

of both rolls are thus equal at this line. The position of the pass relative to the centre-line is important in ensuring that the stock enters and leaves the rolls without difficulty, and the pass should be placed so that any difference in speed between the rolls and the stock is reduced to a minimum.

The position of the pass relative to the pitch line presents little difficulty for sections, such as squares, rounds, etc., which can be rolled in such a position that they are symmetrical about a horizontal line passing through the centre of area of the pass. That is, the pass is so placed that the pitch line coincides with the centre of area. This position, or one very near to it, has been used for the present section in the schedules examined and gives good results.

REDUCTION PER PASS

Whole Section

The number of passes required to reduce a billet to the final pass depends on the reduction in area of the stock in each pass, which should be as great as possible.

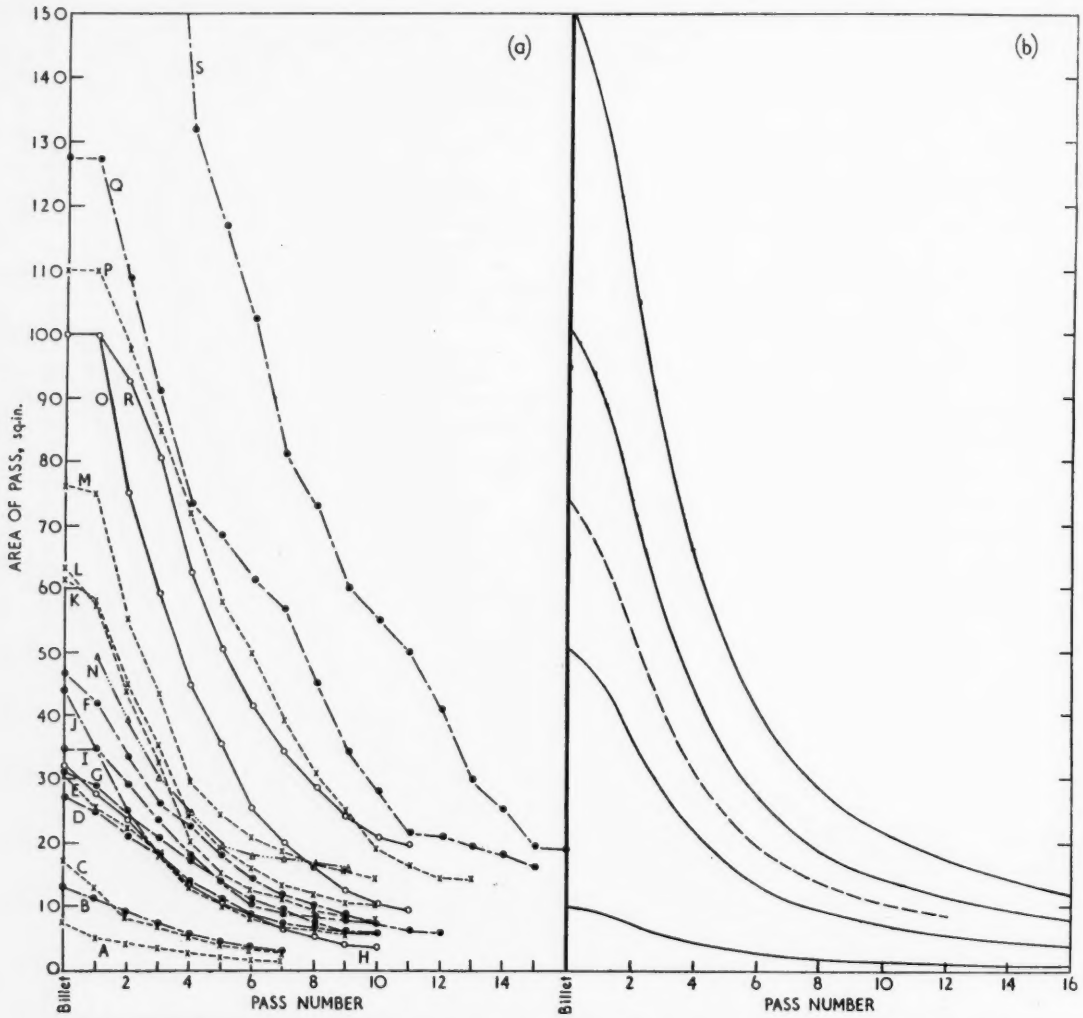

Fig. 11—Area/pass-number curves: (*a*) For each schedule; (*b*) ' smooth ' curves, based on Table III

Table I gives the area of each pass and the percentage reduction in area between any two adjacent passes. In general, the percentage reduction in area per pass is at its greatest between the 2nd and 6th passes, after which it decreases. The reduction in the last pass of a schedule is small, often less than 10%. In several schedules the reduction in the first pass is also small, to make it easier for the stock to enter the rolls, particularly for those schedules in which the rolls are raised and several runs are made through the same pass. The pass is not completely filled in the first run. Area/pass-number curves are plotted for each schedule in Fig. 11*a*, and the average percentage reduction in area per pass is given in Table III. Somewhat greater reductions of about 20–30% are made in the first two passes in those schedules in which the stock is rolled on the diagonal.

'Smooth' curves (Fig. 11*b*), based on Table III and giving the area per pass *vs.* the pass number, do not depart appreciably from those used in the schedules.

The area of the billet required for a particular section depends on the overall dimensions of the beam as well as on its area, as will be seen from Table I. For instance, the 9 in. × 7 in. beam has a greater area but is rolled from a smaller billet than the 12 in. × 5 in. beam.

Figure 12 shows the web and flange dimensions (*A* and *B* in Fig. 1*a*) for the schedules examined, plotted against their corresponding billet dimensions. The points roughly follow two straight lines. An exception is schedule *C*, which is rolled on the diagonal and which illustrates the difference in the method of working the stock in the diagonal and square methods of rolling. Figure 12 can be used to obtain the approximate size of billet for any particular size of beam, or the billet area can be obtained from the formula

$$\text{Billet area} = 1{\cdot}47AB \qquad (1)$$

As an example, suppose it is required to roll a 10 in. × 5 in. beam whose cross-sectional area is 8·85 sq. in. From Fig. 12, a 7 in. × 10½ in. billet would be required. The 7 in. dimension corresponds to the 10 in. web. Figure 11*b* shows a curve for a billet area of 73·5 sq. in. (7 in. × 10½ in.), constructed to the percentage reduction in area per pass schedule suggested above, and 12 passes would be required. A larger billet than that suggested could be used, but more passes would be required. If an area much less than 73·5 sq. in. were used, the number of passes might possibly be no less, because of the necessity to work the stock to the required shape.

Formula (1) is not strictly applicable to diagonal rolling, as the width of the billet is greater than dimension *A* (Fig. 1*a*) of the finished stock, and its height is not much greater than dimension *B*; but the formula may be useful as a first approximation for the area only.

Uniformity of Reduction over the Section

It is desirable that the percentage reduction in area should be uniform over the whole section, so that the elongation of its various parts should be the same; this helps to prevent the loss in the cropped ends which would result from a variable percentage reduction, and to ensure that each pass is completely filled and that the stock is of the required shape. This is particularly important in leader and finishing passes.

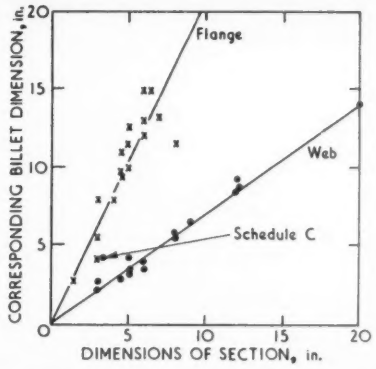

Fig. 12—Graph of web and flange dimensions *vs.* corresponding billet dimensions

For sections, such as beams, which have comparatively long tapered flanges and in which there is little likelihood that metal will be transferred between the various parts of the section (except perhaps at the roots of the flanges), during the passage of the stock through the rolls, underfilling of the pass may occur because of what is known as 'drawing.' If there is unequal percentage reduction in the pass, the stock will tend to take up the length of that part of the section which has been most reduced in the pass. The stock in the other parts of the section will be drawn along with it, and the pass will not be completely filled. As an example, assume that a beam section has a web of, say, 10 sq. in. reduced in area by 50% and elongated to twice its original length. If the flanges are each of 7 sq. in. but are reduced in area by the pass by only 25%, they will elongate by only 33⅓%. However, if the flanges are pulled along by the web their final area will be 3·5 sq .in., as against a pass area of 5·25 sq. in. This is an extreme case, but it emphasizes that all parts of the section should have as nearly as possible the same percentage reduction, otherwise it will be difficult to control the shape of the stock. This is especially important in the passes in the forming and finishing rolls, where the stock is approaching the shape of the required section. The amount of drawing that occurs depends to some extent on the relative areas of the various parts of the section. If the part that is most reduced is small, the other parts may not be drawn along with it and shearing or buckling may occur.

Drawing is not so likely to occur in the roughing passes, as the flanges have a fairly large taper, which makes it easier for metal to move from web to flanges and *vice versa*. Also, it is not so important for the stock completely to fill the early roughing passes. In addition, drawing is less likely to occur in diagonal rolling because it is probably easier than in square rolling for the metal to be transferred between the web and the flanges, although this does not alter the general desirability for equal percentage reduction in the various parts of the section.

The difference in speed, at exit from the rolls, between the stock and the rolls over the periphery

Table IV

DETAILS OF ROLLED STOCK

Schedule	Dimensions of Section, in. × in.	Billet			Length of Stock After Rolling, ft. in.	Rolling Temperature, °C.	
		Cross-Sectional Dimension, in. × in.	Length, ft. in.	Weight, lb.		First Pass	Last Pass
A	3 × 1½	2 11/16 × 2 11/16	16 0	400	94 0	1250	1100
B	3 × 3	5½ × 2⅜	11 6	510	57 6	1100	850
C	3¼ × 3	4¼ × 4¼	11 4	650	70 0	1250	900
D	4½ × 4½	9½ × 2⅞	26 3	2400	138 0	1190	1010
E	5 × 4½	9¾ × 3⅛	23 6	2400	125 6	1200	1000
F	5 × 4½	11 × 4¼	23 0	3550	200 0	1150	900
G	5 × 4½	10½ × 3½	33 0	3360	172 0	1250	1050
H	6 × 3	8 × 4	21 0	2240	190 0	...	...
I	6 × 5	10 × 3½	19 6	2287	94 0	1200	1000
J	8 × 4	8 × 5½	29 0	3470	235 0	1300	900
K	8 × 5	12½ × 5⅝	27 0	5600	200 0	1250	1050
L	8 × 6	13 × 5⅝	29 0	6160	178 0	1250	1050
M	9 × 7	13¼ × 6½	28 0	6720	148 0	1250	1050
N	10 × 6	...	...	...	...	...	...
O	12 × 5	11½ × 8½	9 0	3000	95 0	...	...
P	12 × 6	12 × 9¼	21 0	7880	178 0	1250	1150
Q	12 × 6	15 × 8½	24 8	10,650	100 0*	1120	900
R	12 × 8	11½ × 8½	...	...	...	...	...
S	20 × 6½	15 × 14	14 6	10,650	83 0*	1120	900

* Stock is cut in two during the rolling schedule

of the stock may wear the rolls and mark the stock, because the circumferential speed of a roll changes from the bottom to the top of a groove while the stock is moving at a constant speed. Those parts of the rolls in contact with the web move faster than those parts in contact with the flanges, except in an open pass, where the roll in contact with the outside of the flange moves faster than those parts of the rolls in contact with the web. The variation of circumferential speed over the periphery of the section depends on the ratio H/D, where H is the maximum height of the section in the plane of the rolls and D is the pitch diameter of the rolls. Thus, in this respect it is better to use large-diameter rolls, but care must be taken that the arc of contact is not so long that it increases the roll separating force and torque. In the schedules examined the ratio H/D varies between 0·10 and 0·25, being mostly about 0·16.

In general, the dimensions of the stock are reduced throughout a schedule, but the width (dimension A, Fig. 1*a*) is usually increased in square rolling. The increase in width of the stock, or spread, in a pass is about 3–5% in each roughing pass and about 1% in each pass in the finishing rolls. The width of the stock may be greater than the width of the pass if the stock is rolled on the diagonal as in schedule *C*.

Contraction of Stock After Rolling

Cooling after rolling decreases the dimensions of the stock, and, assuming that its temperature at the last pass is 1000° C., a contraction allowance of 0·014 in./in. should be made to the dimensions of the rolls. However, to increase the life of the rolls the width of the pass may be such that the width of the rolled stock, when the rolls are new, is slightly less than its nominal dimension, *i.e.*, it is the minimum width permitted by the B.S.I. tolerances. Also, as the web is thinner than the flanges it will be at a lower temperature than the flanges at the end of rolling; the contraction of the web along the length of the stock will therefore be less than that of the flanges. To offset unequal contraction, the flanges are sometimes given a slightly greater percentage reduction in the finishing pass. That is, the flanges are elongated more than the web. This also helps to ensure that the pass is completely filled and that the flanges are of the correct shape.

CONCLUSIONS

The schedules analysed cover a wide range of sizes of beams rolled in this country, and it is thought that the above discussion should be helpful when considering the design of new rolls.

Most of the schedules use the square method of rolling, and in only two is the stock rolled on the diagonal. Diagonal rolling, however, appears to have several advantages over square rolling, as less needs to be turned off the rolls when machining them to regain the original pass dimensions; it is easier to reduce the flanges, and there is little tendency for the rolls to grip the stock at exit. Also, ' drawing ' is less likely to occur in diagonal than in square rolling. A disadvantage in diagonal rolling is the occurrence of end thrust, but this may be lessened if the reductions in area of the web and the flanges are carefully adjusted.

In each succeeding pass in a 2-high mill for square rolling, the position of the roll joints relative to the stock is varied either by cross-collaring or by turning the stock between passes. The flanges of a beam rolled in a 3-high mill alternate between the closed and open parts of a pass, without any special steps being necessary. In diagonal rolling the positions of the roll joints are changed by altering the direction of tilt in each succeeding pass in both a 2-high and a 3-high mill.

The pass is usually placed between the rolls so that the centre of area of the section either coincides with or is very close to, usually below, the pitch line of the rolls.

The number of passes in a schedule depends principally on the areas of the billet and the final section. The dimensions, and thus area, of the billet depend on the overall dimensions of the final section. Figures 11*b* and 12 should be helpful in determining the dimensions and area of the billet, the number of passes, and the areas of each pass. The percentage reduction in area per pass should preferably be uniform over the section, to ensure equal elongation of its various parts and complete filling of the pass. Flange height is usually reduced in closed grooves and flange thickness in open grooves.

Roll clearance, including mill spring, must be considered when designing the passes of a schedule, particularly the finishing pass; the contraction of the stock that occurs after rolling must be allowed for in the dimensions of this pass.

APPENDIX

Mills and Rolls

Table II gives operating details of the mills and rolls. There is a large variation between schedules in the total tonnage rolled by each set of rolls, the tonnage rolled between dressings, and the rate of production. In general, they all depend on the size of the section rolled; the roll material and layout of the mill are also important, but there are not enough data to draw any conclusions in this respect. The reduction in diameter at a dressing does not exceed $\frac{1}{2}$ in., irrespective of the roll diameter.

The ratio L/D (*i.e.*, the length to the pitch diameter of the rolls) is given, the average being about 2·5. If this value is used in a new design, the rolls should not deflect unduly during rolling.

The B.S.I. permitted tolerances on the length of the web (dimension A, Fig. 1*a*) are $-\frac{1}{32}$ in. to $+\frac{1}{8}$ in. The increase in width of the finishing pass at discard, for the sections examined, varies from $\frac{1}{8}$ in. to $\frac{1}{4}$ in.

Rolled Stock

Table IV gives details of the rolled stock. The dimensions of the billet do not coincide for every schedule with the billet areas listed in Table I, as the billet is not always rectangular. Also, in schedules Q and S the stock is cut in two during rolling.

The maximum possible length of the stock depends on several factors, including the size of the cogging mill and the dimensions of the reheating furnace if the stock is not rolled directly from this mill.

Acknowledgments

The author wishes to thank the members of the Roll Design Conference for their helpful discussions, especially Mr. P. Davies of the Steel Company of Wales Ltd., Mr. T. Davison of the Lanarkshire Steel Co., Ltd., Mr. J. Dougan of the Skinningrove Iron Co., Ltd., Mr. D. Dyson of C. Akrill and Co., Ltd., Mr. J. Jones of the Darlington and Simpson Rolling Mills Ltd., Mr. R. Knox of Dorman Long and Co., Ltd., Mr. B. Robinson of the Park Gate Iron and Steel Co., Ltd., and Mr. H. Williams, lately retired from the Cargo Fleet Iron Co., Ltd., and their Companies, for permission to publish their roll-pass schedules.

Correspondence on the Paper—

TENSILE AND IMPACT PROPERTIES OF HIGH-PURITY IRON–CARBON AND IRON–CARBON–MANGANESE ALLOYS OF LOW CARBON CONTENT*

By N. P. Allen, W. P. Rees, B. E. Hopkins, and H. R. Tipler

Mr. **E. Wood** and Mr. **P. L. Lewis** (Midland Research Company Ltd.) wrote : We have been very interested in this and the earlier work from the N.P.L.[1,2] on pure iron with amounts of added elements, and we find that the results are capable of direct application to wrought iron and the low-carbon rimmed steels hitherto used for chain making. It has been our experience, both in the laboratory and the field, that carbide films are at least as serious in promoting brittleness in mild steel[3] as strain ageing ; when the two are combined the resulting brittleness can be unbelievable. We have had $\frac{1}{2}$-in. dia. rimmed-steel chain break from the impact produced by letting it run through the hands on to a stone floor.

We have met all the types of structure shown in the paper in both wrought iron and mild steel and, although it is true that material with less than 0·06% of carbon is more prone to film formation, we have had the worst examples, from the point of view of complete films and equally complete brittleness, with carbon contents greater than 0·10%. When thermal-treatment conditions coincide with certain mechanical conditions and critical grain size, the whole of the grains can be surrounded by a continuous film of carbide of appreciable thickness. In practice, fortunately, the film is usually not continuous. Figure *A* shows carbide films in wrought iron containing 0·12% of carbon. This was taken from a $\frac{5}{8}$-in. chain, broken in service, immediately after periodic annealing. This treatment, of course, is supposed to restore ductility,[4] but this chain was annealed at 700° C. The links, when squeezed in a vice, could be clearly heard to give a distinct crepitation at the first sign of yield, followed by total brittle failure. Normalizing from 950° C. completely restored the properties. We believe that the widely used and statutorily respectable periodic annealing of wrought iron at intermediate temperatures of 650–720° C. can itself promote brittleness.

The best temperature in our view is 600–650° C., although Jeffrey[5] gives 700° C., a temperature which we have found to be quite unsuitable. It is better to

J. Iron Steel Inst., 1953, vol. 174, pp. 108–120.

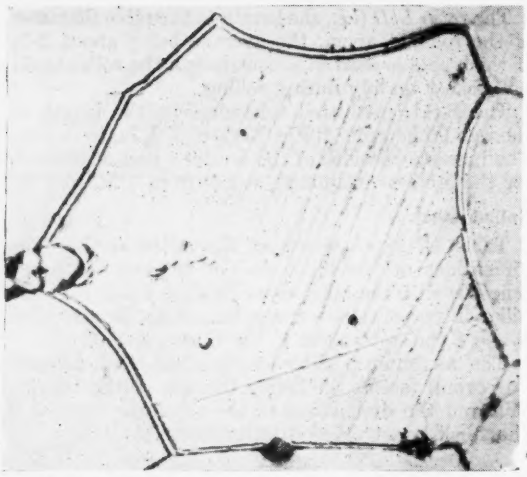

Fig. A—Carbide films in 0·12% C wrought iron

normalize, preferably in a controlled atmosphere or salt bath ; when the latter is not available we recommend 600–650° C. for not more than three annealings, with full normalizing at every fourth annealing. The whole problem in relation to wrought iron is at present under investigation in our laboratory.

It seems to us that brittleness from carbide films has often been reported as, and confused with, strain-age embrittlement and/or surface embrittlement from work-hardening, and our work leaves us in no doubt that in both wrought iron and mild steel it is at least as important as these effects.

We agree that the rate of cooling from the austenitizing temperature is important in promoting carbide films—we are currently concerned with an example in as-rolled mild steel in which carbide films appear to be affecting machinability adversely—but the effects of prolonged or repeated intermediate annealings and of prior thermal and mechanical history[6] should not be overlooked.

The inhibiting effect of manganese on both film formation and the tendency to ageing is welcome authoritative confirmation of properties which have long been recognized in practice by the increasing use of 1½% manganese steel for chain and lifting gear.[7] There is everything to be said for this steel for both ordinary[8] and higher-tensile[9] steel chain (although the carbon content needs to be raised for the latter), especially when the low transition temperature is also considered.

An interesting aspect of the problem which we have lately met is that otherwise good, fully-killed steel containing 0·30% of carbon and 0·70% of manganese can fail under certain conditions in a completely brittle manner owing to the presence of a 0·010–0·020-in. decarburized layer, which can show both carbide films and/or strain ageing and can set up cracks that are propagated more or less deeply into the 'core'. Ordinary notched-bar tests fail, obviously, to reveal this effect. Recognition of it has proved to be most useful in investigating problems of cracking when cold-bending mild steels under production conditions. We are quite satisfied that an appreciably harder but normalized material is better for cold-bending than steel which has been carefully softened by intermediate annealing at about 700° C.

We are most interested in the explanation put forward for the brittle behaviour of ostensibly ductile ferrite with films of carbide present. It seems to be true (as the crepitation mentioned above supports) that a large number of small cracks appear in the carbide at slight deformation, and the presence of a greater or lesser degree of triaxial stress in the ferrite at the roots of the notches offered by the cracks in the carbide may very well be true. When a brittle wrought-iron or mild-steel fracture in the presence of carbide films is plated and examined at high magnification, the fracture can be seen to be not wholly intergranular, and small branch cracks in the ferrite can invariably be seen. But might precipitation occur on preferential planes of the ferrite ?

AUTHORS' REPLY

Dr. **N. P. Allen** and his co-workers wrote in reply : We are pleased to have confirmation of the importance of the effects of carbide films at grain boundaries in wrought iron and mild steel from Mr. Wood and Mr. Lewis. It appears from their discussion that the frequency of the occurrence of these films is such that careful attention should be paid to heat-treatment procedures. We agree that for such components as wrought-iron chains a periodic normalizing treatment is preferable to annealing below A_1 to obtain maximum resistance to impact loading. This was in fact pointed out by Gough and Murphy[4] in their investigations of the causes of failure of wrought-iron chains in 1928 but, in view of the conditions under which heat-treatments had to be carried out and the tendency for scaling to occur along scarf welds, it was agreed at that time that it was advisable to apply a subcritical anneal rather than a normalizing treatment. Gough and Murphy do not appear to have encountered brittleness due to grain-boundary carbide films, possibly because the carbon contents of their wrought irons were low ; there does not seem to be any carbide in their photomicrographs. Under present conditions it may well be practicable for at least some of the periodic heat-treatments to consist of normalizing, and for this to be done either in a controlled atmosphere or, in cases where the gear being treated is not too large, in salt baths ; Jeffrey[5] recommends this procedure. Where subcritical anneals are applied, we agree that it is important to avoid the formation of grain-boundary carbide films, and the best temperature to use in a particular case needs some consideration. This emphasizes the need for good technical control.

The effect of manganese (and other elements, according to Görrissen[3]) in decreasing and eventually eliminating the formation of carbide films has been noticed in practice (*e.g.*, in the 1½% Mn steel used for chains), but we were not aware that the effect of manganese in decreasing the quench-ageing tendency had been previously established. The 1½% Mn steel has a reduced tendency to strain age, but this could have been attributed to other reasons than the effect of manganese itself.

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Activity Coefficients of Oxygen and Phosphorus in Iron–Oxygen–Phosphorus Melts

By J. Pearson, Ph.D., M.Sc., F.R.I.C., and E. T. Turkdogan, Ph.D., M.Met.

SYNOPSIS

Molten Fe–O–P alloys have been equilibrated at temperatures between 1572° and 1624° C. with hydrogen/water-vapour mixtures of known composition. Thermal segregation in the gas phase was avoided by the use of a preheater and the admixture of argon. The activity coefficients of oxygen and phosphorus in the ternary melts are reduced, compared with those in the binary Fe–O and Fe–P systems, by factors which depend on the phosphorus and oxygen contents, the factors being given by the equations

$$\log f_O^P = -0{\cdot}032\,[P\,\%] \text{ and } \log f_P^O = -0{\cdot}062\,[O\,\%].$$

In ternary melts Fe–*X*–*Y*, the value of $\partial \log f_X^Y / \partial [Y\,\%]$ is related to the free energy of formation of the compound between *X* and *Y* from the elements in solution. The activity coefficients are reduced when the free energy is strongly negative and raised when the free energy is markedly positive, compared with those in the binary systems. 824

THE interaction between solutes in liquid iron, as indicated by a change of activity coefficient of one solute on adding another, has been studied in the following systems: C–S, C–Si, C–Cr, O–C, O–V, O–Cr, O–Al, O–Si, S–Si, S–P, and S–Mn,[1–13] and some information is available on the reason why activity coefficients change as they do.[14] The P–O system has not been investigated from this point of view, although Bookey, Richardson, and Welch[15] have suggested that oxygen may lower the activity coefficient of dissolved phosphorus.

In view of the technological importance of the possible mutual effects of oxygen and phosphorus in molten iron on their respective activity coefficients, it was decided to investigate the interaction more fully.

EXPERIMENTAL DETAILS

The experimental technique used was essentially that of equilibrating an iron–phosphorus melt with a hydrogen/water-vapour mixture of known composition, quenching the melt, and analysing it for oxygen and phosphorus. The composition of the gas phase was such that no slag was formed; it was thus possible to vary the oxygen and phosphorus contents independently over a reasonable range.

Furnace—A vertical section of the reaction tube is shown schematically in Fig. 1. The prism served merely to inspect the contents of the tube during the experiments. The cone carrying the prism could be removed for sampling and charging purposes. Two Pt/Pt–13%Rh thermocouples were used, the hot junctions being frequently renewed. The bottom thermocouple, for checking the temperature distribution, was installed mainly in case the upper one failed during an experiment. The upper thermocouple could serve, if vertically displaced, to measure the temperature of the preheater. The latter was 12 in. long and 0·5 in. dia. The temperature of the furnace was controlled to ± 3° C. in the range 1500–1650° C. by a Kent automatic controller, the overall error in control and measurement being approximately ± 5° C.

Gas Train—The gas train and apparatus for preparing the hydrogen/water-vapour mixtures were similar to those used by Bookey and co-workers,[15] but provision was made for introducing argon into the gas stream. The argon was purified by passage over calcium metal heated to 700° C., and the efficiency of the calcium treatment was checked periodically with an oxygen detector.[16]

Sampling and Charging—Samples were taken using a silica-tube Taylor sampler, the reaction tube being flushed with argon before and during sampling. It was possible to complete the withdrawal of a sample within one minute of turning off the hydrogen/water-vapour. Surface oxidation of the samples during cooling was prevented by quenching them in cold water while still in the silica tube. Any sample which became superficially oxidized as a result of the slowness of this operation was discarded. In many cases the experiment was continued after sampling by adding fresh charge material from the top. In this way, the phosphorus content of the molten alloy could be varied by the use of appropriate iron–phosphorus additions.

Materials—The pure iron used had the following composition: 0·008% C, 0·002% Si, 0·005% Mn, 0·008% S, 0·001% P, 0·01% Ni, 0·001% Cr, 0·006% Cu, 0·001% Al. An iron–phosphorus alloy, prepared in the B.I.S.R.A. Chemistry laboratory[15] and containing about 10% of phosphorus, was used to bring the charge of a total weight of 80–100 g. to the desired phosphorus content.

Chemical Analysis—Phosphorus estimations were carried out by the Metallurgy (General) Division of B.I.S.R.A. at the Bragg Laboratories, Sheffield. Oxygen contents were determined by vacuum fusion on samples weighing 2–3 g. Estimations were in duplicate and, in the range 0·02–0·03% of oxygen,

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Dr. Pearson is Head of the Chemistry Department and Dr. Turkdogan is Head of the Physical Chemistry Section of the Chemistry Department of the Association.

Table I

STUDY OF THERMAL DIFFUSION

Sample No.	Temperature, °C.	$\frac{P_{H_2O}}{P_{H_2}}$	Oxygen, wt.-%	Log K_O	Preheater Temperature, °C.	Argon, ml./min.	Hydrogen, ml./min.
A1	1550	0·1049	0·0138	0·881	—	Nil	200
A2	1550	0·1049	0·0181	0·763	1300	Nil	200
A3	1615	0·1055	0·0246	0·636	—	188	188
A4	1564	0·1062	0·0240	0·646	1500	Nil	200
A5	1625	0·1062	0·0300	0·549	1500	160	200

agreed to within 0·002% and in many cases to within 0·0006%. At higher oxygen contents (0·045–0·050%), agreement between duplicates was within 0·004%.

RESULTS

Preliminary Experiments

To check the gas-tightness of the apparatus and the suitability of the sampling technique, two pure-iron melts were held at 1600° C. for 24 hr. in a dry hydrogen–argon mixture. Samples were analysed for oxygen and aluminium, the mean results being [O] = 0·0034% and [Al] = 0·0025%. These values, which are in good agreement with those of Gokcen and Chipman[9] on the aluminium–oxygen equilibrium in iron in contact with solid alumina, indicated the satisfactory functioning of the apparatus and the absence of oxidation during sampling. Since the actual experiments were to be conducted under relatively high water-vapour/hydrogen ratios, it was presumed that contamination of the melts by aluminium would be much less than that indicated above.

If the gas mixtures in equilibrium with the melts are to be the same as those led into the furnace, thermal segregation must be avoided. In view of the detailed study by Dastur and Chipman,[17] only sufficient experiments to check their findings were carried out. The results are given in Table I and plotted in Fig. 2, in which the straight line represents the findings of Dastur and Chipman. Using a flow-rate of 200 ml./min., it was shown that segregation was excessive when there was no preheating of, nor argon in, the mixture. Segregation was reduced appreciably if the preheater ran at 1300° C. or if argon at 200 ml./min. was added. Complete elimination of segregation was achieved with the preheater at 1500° C. in the presence or absence of argon. The oxygen contents of pure iron so obtained at two temperatures (1563° and 1625° C.) were in agreement with those of Dastur and Chipman.[17] For additional safety, the preheater was held at 1600° C. and argon in the above proportions was used during subsequent experimental runs.

Iron–Phosphorus–Oxygen Melts

The results of 18 experiments, most of which were carried out at 1600° C., are given in Table II. It was found that a period of less than 15 min. was required to establish equilibrium between the metal and gas phases. This is illustrated by results *B*12 and *B*13. The former sample was taken 10 min. after the addition of pure iron to a previous melt, and the latter sample was taken after a further period of 2 hr., no alteration having been made to the charge or to the gas mixture. Nevertheless, a period of 2 hr. between charging and sampling was normally allowed. Sample *B*5 was also taken 2 hr. after *B*4, without change of conditions except a slight temperature rise. The phosphorus contents of these two samples and of *B*12 and *B*13 show that the charges were homogeneous at the time of sampling.

It was intended originally to carry out experiments with a number of hydrogen/water-vapour ratios, but in view of the smallness of the interaction between phosphorus and oxygen, two ratios only were used.

Effect of Phosphorus on the Activity Coefficient of Dissolved Oxygen

The results of Dastur and Chipman[17] show that in the liquid iron–oxygen binary system the activity of dissolved oxygen is proportional to its percentage content by weight, up to the limit of solubility. If the activity in very dilute solutions is represented by the percentage weight, the activity coefficient f_O° is unity over the range of the iron–oxygen solution.

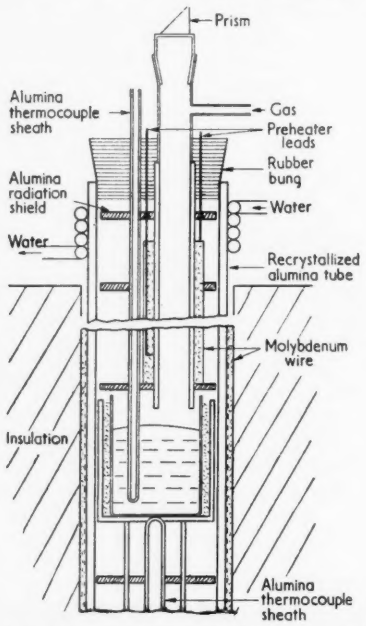

Fig. 1—Furnace assembly (not to scale)

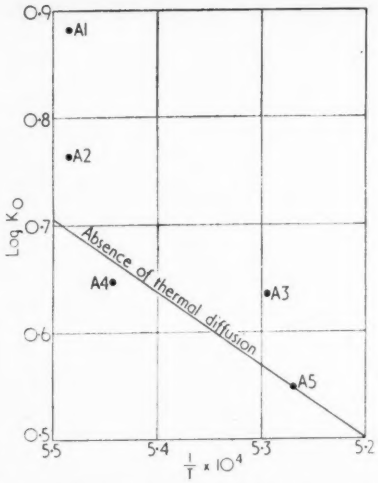

Fig. 2—Effect of thermal diffusion on log K_O

The relationship between the hydrogen/water-vapour ratio and the oxygen content of pure iron is given by Dastur and Chipman[17] as:

$$K_O = \frac{p_{H_2O}}{p_{H_2}[O\%]} \quad \ldots\ldots(1)$$

where

$$\log K_O = \frac{7050}{T} - 3{\cdot}17 \quad \ldots\ldots(2)$$

In the presence of dissolved phosphorus the value of K_O from equation (1), now written K'_O, will differ from that calculated from equation (2) if the phosphorus changes the activity coefficient of the oxygen. The results in Table II show that K'_O is less than K_O, and this indicates that the activity coefficient of oxygen, in the presence of dissolved phosphorus, is reduced by a factor f_O^P less than unity, because

$$\log f_O^P = \log K'_O - \log K_O \quad \ldots\ldots(3)$$

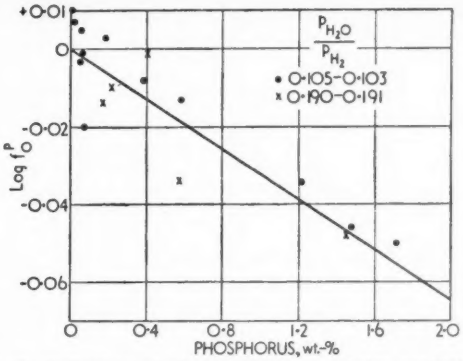

Fig. 3—Influence of phosphorus on activity coefficient of oxygen dissolved in iron

In Fig. 3, log f_O^P is plotted against the percentage weight of phosphorus in the melts. The scatter of the points is well within the experimental error, since a change of 0·0005% in the analysed oxygen content would make a difference of 0·005 in the value of log f_O^P. The straight line drawn through the points and the origin may be represented by the following equation:

$$\log f_O^P = -0{\cdot}032\,[P\%] \quad \ldots\ldots(4)$$

and this equation appears to be independent of the oxygen content, at least over the range 0·025–0·050%, and of temperature over the range 1572–1624° C.

Effect of Oxygen on the Activity Coefficient of Dissolved Phosphorus

On the assumption that the concentrations of oxygen and phosphorus in the alloys studied are very low, the effect of oxygen on the activity coefficient of phosphorus may be obtained from the relationship derived by Wagner,[18] which in this case takes the form:

$$\frac{\partial \log f_O}{\partial [P\%]} = \frac{\partial \log f_P}{\partial [O\%]} \times \frac{16}{31} \quad \ldots\ldots(5)$$

Table II

Fe–P–O MELTS EQUILIBRATED WITH $H_2 + H_2O$ GAS MIXTURES

Sample No.	Temperature, °C.	$\frac{p_{H_2O}}{p_{H_2}}$	Phosphorus, wt.-%	Oxygen, wt.-%	Log K'_O	Log K_O	Log f_O^P	f_O^P
B1	1600	0·1053	1·71	0·0301	0·544	0·594	−0·050	0·893
B2	1600	0·1053	1·47	0·0298	0·548	0·594	−0·046	0·900
B4	1624	0·1053	1·21	0·0323	0·512	0·546	−0·034	0·925
B5	1600	0·1032	1·21	0·0291	0·550	0·594	−0·044	0·904
B7	1592	0·1030	0·585	0·0261	0·596	0·609	−0·013	0·971
B8	1589	0·1030	0·386	0·0254	0·608	0·616	−0·008	0·982
B9	1596	0·1030	0·180	0·0256	0·606	0·602	+0·003	1·001
B10	1600	0·1035	0·069	0·0276	0·574	0·594	−0·020	0·955
B11	1600	0·1035	0·060	0·0264	0·593	0·594	−0·001	0·998
B12	1600	0·1037	0·050	0·0266	0·591	0·594	−0·003	0·993
B13	1600	0·1037	0·050	0·0261	0·599	0·594	+0·005	1·001
B15	1600	0·1049	0·012	0·0263	0·601	0·594	+0·007	1·002
B16	1600	0·1048	0·006	0·0261	0·604	0·594	+0·010	1·003
C4	1574	0·1912	1·45	0·0480	0·600	0·648	−0·048	0·895
C5	1572	0·1912	0·569	0·0462	0·617	0·651	−0·034	0·925
C6	1600	0·1907	0·401	0·0487	0·593	0·594	−0·001	0·998
C7	1600	0·1907	0·207	0·0497	0·584	0·594	−0·010	0·977
C8	1600	0·1907	0·166	0·0502	0·580	0·594	−0·014	0·968

In discussing ternary solutions, such as Fe–X–Y, it should be borne in mind that an activity coefficient f_X may be regarded as a combination of the activity coefficient f_X^X, in the binary system Fe–X of the same concentration of X, and the factor f_X^Y, which indicates the magnitude of the interaction between X and Y, *i.e.*, the change in the activity coefficient on adding a given amount of Y to the binary solution Fe–X. Thus, according to Wagner,[19]

$$f_X = f_X^X \times f_X^Y \quad \ldots\ldots(6)$$

If equation (4) is differentiated with respect to [P%], the following expression is obtained:

$$\frac{\partial \log f_0^P}{\partial [P\%]} = -0{\cdot}032 = \frac{\partial \log f_O}{\partial [P\%]}, \quad \ldots\ldots(7)$$

since $f_0^0 = 1{\cdot}0$ in binary Fe–O melts. Combination of equations (5) and (7) gives:

$$\frac{\partial \log f_P}{\partial [O\%]} = -0{\cdot}032 \times \frac{31}{16} \quad \ldots\ldots(8)$$

or

$$\partial \log f_P = -0{\cdot}062\, \partial [O\%] \quad \ldots\ldots(9)$$

Integrating equation (9):

$$\log f_P = -0{\cdot}062[O\%] + C \quad \ldots\ldots(10)$$

When $[O\%] = 0$, $\log f_P = \log f_P^P$, and hence

$$\log f_P^0 = \log f_P - \log f_P^P = -0{\cdot}062[O\%] \quad \ldots(11)$$

The factor f_P^O appears to be independent of phosphorus content, at least in the melts studied.

An attempt was made to evaluate the influence of phosphorus concentration on the value of f_P^P, using equations (4) and (11) and the experimental findings of Bookey, Richardson, and Welch,[15] and although no firm conclusion can be drawn it does appear that the activity coefficient of phosphorus increases with concentration in the binary Fe–P solution, as is the case in Fe–Si and Fe–C solutions.

DISCUSSION

In view of the smallness of the phosphorus–oxygen interaction in molten iron, it is desirable to examine the conclusions reached by Bookey, Richardson, and Welch.[15] In their experiments they equilibrated molten Fe–P alloys with solid lime and tetracalcium phosphate under H_2/H_2O mixtures. At low oxygen activities, and therefore low oxygen and high phosphorus concentrations in the melt, they found that $\log(p_{H_2O}/p_{H_2})$ was linearly related to log[P%], but that when the oxygen concentration was greater and the phosphorus concentration smaller there was a deviation from the linear relationship. This was attributed to the effect of oxygen on the activity coefficient of phosphorus. If this were indeed the case the slopes of equations (4) and (11) should be at least 100 times greater than those obtained. It is suggested that it is not permissible to assume that phosphorus in iron obeys Henry's law up to concentrations of 1%.

It has been pointed out recently by Gokcen and Chipman[9] that there is a parallelism between the interactions of aluminium, vanadium, and chromium with oxygen dissolved in molten iron and the free energy of formation of the respective oxides from the dissolved components. It appears to be worthwhile to examine this parallelism more closely and to ascertain whether it holds for the effects of alloy additions on elements other than oxygen.

When comparing elements of different valencies, the use of the free energy of formation per g.mole of compound or per g.atom of a dissolved element is unsatisfactory, because it involves the combination of different numbers of atoms. It appears more logical to use the concept of free-energy change per mean g.atom, defined in the following way:

Let the reaction considered be

$$a\underline{X}(1\%) + b\underline{Y}(1\%) = X_aY_b \quad \ldots\ldots(12)$$

with a free-energy change of ΔG_T per g.mole. Then the free-energy change per mean g.atom is

$$\overline{\Delta G}_T = \Delta G_T/(a+b) \quad \ldots\ldots(13)$$

The best measure of the interaction between two solutes is $\partial \log f_X^Y/\partial [Y\%]$, which, following Gokcen and Chipman,[9] may be designated e_X^Y. The coefficient e_X^Y may be regarded as the factor by which 1% of one alloying element alters the activity coefficient of another present in the same solution. Needless to say, it will not always be possible to obtain as much as 1% of all alloying elements in solution, nor might they obey the Wagner relationship if it were, but the above represents a simple way of considering the meaning of e_X^Y.

Table III lists the values of $\overline{\Delta G}_{1873°K.}$ for a number of oxides, sulphides, and carbides, together with the corresponding magnitudes of e_X^Y, *i.e.*, the effect of the alloying element on the activity coefficients of dissolved oxygen, sulphur, or carbon. The last column in Table III gives the sources from which the data used in evaluating $\overline{\Delta G}_T$ and e_X^Y were obtained. It should be stressed that, generally, e_X^Y is constant only at low concentrations of Y and then approaches zero as the concentration increases. The results used in evaluating e_X^Y were such that the slope of the $\log f_X^Y/[Y\%]$ relationship could be taken as constant.

Table III

VALUES OF $\overline{\Delta G}_{1873°K.}$, kg.cal. per mean g.atom

Compound	State of X_aY_b at 1873° K.	$\overline{\Delta G}_{1873°K.}$	e_X^Y	Reference No.
Al_2O_3	Solid	−23·4	−12·0	9
SiO_2	,,	−13·7	−0·87	10
CO	Gas	−10·5	−0·28	17, 20, 14
V_2O_3	Solid	−10·0	−0·25	7
Cr_2O_3	,,	− 6·4	−0·06	8
MnO	,,	− 4·9	0·0	17, 20, 21
P_2O_5	(Liquid)*	+11·5	−0·032	22
MnS	Solid	+ 2·4	−0·026	20, 23, 13
CS_2	Gas	+16·3	+0·10	20, 23, 14
SiC	Solid	+15·2	+0·093	10, 17, 14
$Cr_{23}C_6$	,,	+ 2·0	−0·020	14, 5

* $\overline{\Delta G}_{1873°K.}$ was calculated for P_2O_5 in the liquid state.

In Fig. 4, e_X^Y is plotted against $\overline{\Delta G}_{1873°K.}$. With the exception of Mn–O, all points for oxides lie on a smooth curve. This curve shows that the addition of a hypothetical 1% of one solute affects the activity coefficient of a second solute by an amount depending on the tendency of the two solutes to combine, as measured by the value of $\overline{\Delta G}_T$. When the absolute value of $\overline{\Delta G}_T$ is small, the effect of the first solute on the activity coefficient of the second is small also. As $\overline{\Delta G}_T$ becomes increasingly negative, the activity coefficient of the second solute is lowered to a progressively greater extent. The points for Cr–C, Si–C, Mn–S, and C–S indicate that when $\overline{\Delta G}_T$ becomes markedly positive the activity coefficients are increased by a factor which increases with $\overline{\Delta G}_T$. The solutes thus tend not to combine with but to repel each other. It is not suggested that all the points in Fig. 4 lie on one curve, as they relate to the effect of 1% of an alloy addition on f_X^Y. To derive a general relationship it would be necessary to examine ε_X^Y, *i.e.*, $\frac{\partial \ln \gamma_X}{\partial N_Y}$, where γ_X is the activity coefficient referred to pure X as a standard state and N_Y is the atom fraction of Y in the solution.

Figure 4 may be used to determine the value of f_X^Y at any small concentration of Y, but unless the activity coefficient f_X^X in the binary Fe–X solution is known it is not possible to calculate the activity coefficient f_X in the ternary Fe–X–Y solution. When f_X^X is known as a function of the concentration of X, calculation of f_X is permissible.

CONCLUSIONS

Phosphorus dissolved in molten iron reduces the activity coefficient of oxygen to a small extent only, the factor being given by

$$\log f_0^P = -0{\cdot}032\,[P\%].$$

Because the activity coefficient f_0^o of oxygen in binary Fe–O melts is unity, it is also possible to write

$$\log f_O = -0{\cdot}032\,[P\%].$$

Using the modified form of Wagner's relationship, the influence of oxygen on the activity coefficient of phosphorus has been calculated to be:

$$\log f_P^O = -0{\cdot}062\,[O\%],$$

but lack of information prevents the evaluation of $\log f_P^P$ in binary Fe–P melts.

The interaction between solutes, indicated by the magnitude of the change of activity coefficient on adding a second solute to a binary melt, depends on the free energy of formation of compounds between them. The more negative the free energy of formation from the dissolved elements, the greater is the mutual lowering of activity coefficients. If the free energy of formation is markedly positive, activity coefficients are raised as compared with those in binary solutions.

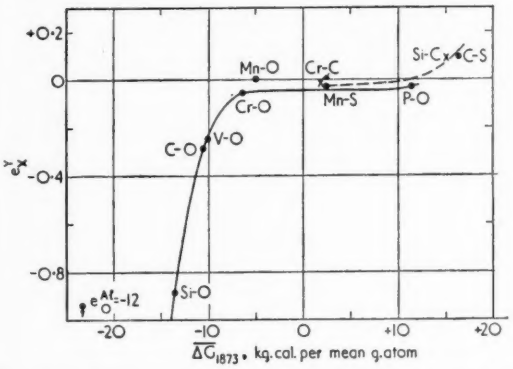

Fig. 4—Relationship between $\overline{\Delta G}_T$ and e_X^Y at 1600° C.

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Diffusion of Nitrogen in Iron

By J. D. Fast and M. B. Verrijp

SYNOPSIS

Diffusion coefficients of nitrogen in α-iron at 500° and 600° C. are derived from the desorption rates of nitrogen from iron wires in hydrogen, using internal friction measurements to determine concentration ratios. Extrapolation to 21·5° and 9·5° C. gives values of D that correspond well with those calculated from internal friction measurements at these temperatures and thus strongly support Snoek and Polder's interpretation of damping caused by carbon and nitrogen. The combined measurements yield for the diffusivity of nitrogen in α-iron

$$D_N(\alpha) = 6{\cdot}6 \times 10^{-3}\, e^{-18{,}600/RT} \text{ sq. cm./sec.}$$

Determination of the diffusion coefficient of nitrogen in γ-iron at 950° C. shows that diffusion in γ-iron is much slower than in α-iron. 804

Introduction

TECHNICAL steels always contain small quantities of nitrogen. The solubility of nitrogen in austenitic steels is so great that the presence of small quantities of this element is not harmful, and in exceptional cases is even favourable, because nitrogen stabilizes the γ phase. In ferritic steels, however, the solubility of nitrogen is so small that its presence is always harmful, except in those cases where it is intentionally introduced to produce surface hardening. The deleterious ageing phenomena caused by nitrogen in ferritic steels are well known. To anticipate the occurrence of these phenomena the solubility and the diffusion coefficient of nitrogen in α-iron must be known as functions of temperature.

This paper gives the results of measurements of the diffusion coefficient ; those of the solubility will be given in a future paper. For comparison with the values for α-iron the diffusion coefficient of nitrogen was also determined for γ-iron at one temperature (950° C.).

In all measurements use was made of the internal friction caused by nitrogen dissolved in α-iron. This internal friction may briefly be explained as follows.[1, 2, 3] The solid solution of nitrogen in α-iron is disordered for zero stress. On the application of a unidirectional stress a redistribution of the nitrogen atoms will, in general, take place. The relaxation time τ for this redistribution is determined by the jump frequency of the nitrogen atoms and, as a consequence, τ obeys the equation

$$\tau = \tau_0 e^{U/RT} \qquad \text{.....(1)}$$

where T is the absolute temperature, R is the gas constant, and U is the activation energy for the diffusion of nitrogen atoms. Thus, for an applied stress σ, the corresponding strain ε is made up of two parts : $\varepsilon = \varepsilon' + \varepsilon''$, where the time-independent quantity ε' is the perfectly elastic strain given by $\varepsilon' = \sigma/E$ (E = unrelaxed modulus of elasticity), and where the time-dependent quantity ε'' is the anelastic strain. The final value of ε'' may be written as

$$\epsilon''_f = \Delta \,.\, \epsilon' = \Delta \cdot \frac{\sigma}{E} \qquad \text{.....(2)}$$

This shows that the magnitude of the anelastic effect is given by a constant Δ, called the relaxation strength. According to Polder[2] and Dijkstra[4] the relaxation strength Δ is proportional to the concentration of the interstitially dissolved atoms if the concentrations are so small that interaction between these atoms may be neglected. The influence of temperature on Δ will be mentioned in a later section.

In the experiments polycrystalline iron wires were used with nitrogen concentrations so small that Δ was always much smaller than unity and proportional to the nitrogen concentration.

Owing to the anelastic effects, strain lags behind stress when a periodically varying stress is applied to the metal. For $\Delta \ll 1$, the phase angle (loss angle) β, which is a measure of internal friction, is given by

$$\beta = \Delta \cdot \frac{\omega\tau}{1 + \omega^2\tau^2} \qquad \text{.....(3)}$$

where ω is the angular frequency of the mechanical oscillation. Equation (3) represents the internal friction as a function of ω and τ (*see* equation (1)). The maximum value of the internal friction is at $\omega\tau = 1$. If, for instance, the internal friction of α-iron containing a small quantity of nitrogen (say, 0·1 at.-%) in solid solution is measured at constant frequency as a function of temperature, a sharp maximum is found at a well defined temperature (21·5° C. for a period of oscillation $T = 1{\cdot}3$ sec.). The experimentally observed variation of internal friction with temperature is closely represented by equation (3), with τ given by equation (1), if nitrogen (or carbon) is virtually the only impurity in the iron.

SPECIMENS AND EXPERIMENTAL METHODS

Iron was obtained in a very pure state by high-frequency melting and casting in a good vacuum.[5] The cast rod had a diameter of 14 mm. and was transformed into 0·7-mm. dia. wire by cold swaging and cold drawing. About 0·10 at.-% of nitrogen was introduced into 300-mm. lengths of the iron wire by heating them for 3 hr. at 950° C. in a gas stream of the composition 99 vol.-% N_2 + 1 vol.-% H_2. The gas mixture was purified by passing it over heated copper turnings and subsequently through traps cooled in liquid nitrogen. After loading with nitrogen the wires were quenched in water, heated for 10 min. at 560° C. in pure nitrogen, and again quenched in water. The final grain size was about one-tenth of the diameter of the wire. X-ray examination showed the grains to have random orientations.

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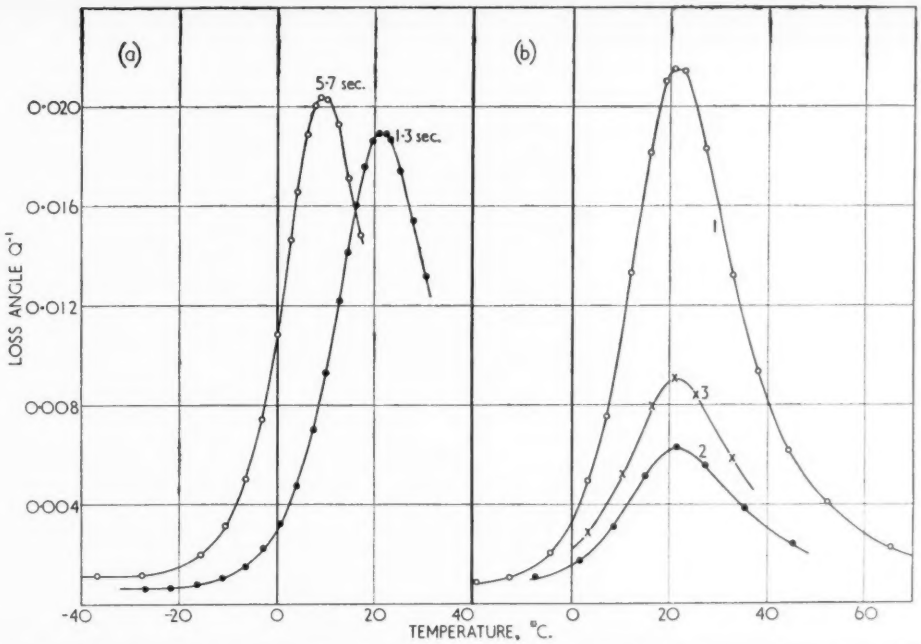

Fig. 1—Internal friction peaks of an iron wire. (*a*) Wire containing nitrogen, as measured with periods of oscillation of 1·3 and 5·7 sec. (*b*) Wire after (1) loading with nitrogen; (2) 15 min. at 600° C. in hydrogen and W.Q.; (3) homogenizing at 560° C. in nitrogen and W.Q.

Immediately after the last quench the internal friction peak was determined by measuring the internal friction of the wires at different temperatures between −20° and 60° C. For this purpose they were used as the suspension element in a torsional pendulum system with a period of oscillation of 1·3 or 5·7 sec. The logarithmic decrement was determined during free decay of the torsional oscillations. The loss angle β (often represented by the symbol Q^{-1} by analogy with electrical circuits) is found by dividing the logarithmic decrement by π. The apparatus used differed little from that described by Kê.[6]

The diffusion coefficient of nitrogen at the temperature of maximum damping can be calculated from the time of relaxation (*see* next section). The diffusion coefficients at 500°, 600°, and 950° C. were determined by studying the rates of desorption of nitrogen.

DIFFUSION COEFFICIENTS AT 9·5° AND 21·5° C.

By considering the diffusion of interstitial solute atoms in a body-centred cubic metal as a random walk problem, the diffusion coefficient is easily shown to be given by $D = \lambda^2/6\tau'$, where λ is the distance between nearest neighbour interstitial positions (jump length) and τ' the mean time of stay of an atom at a given lattice site. As λ is only half the lattice constant a,

$$D = \frac{1}{24}\cdot\frac{a^2}{\tau'} \qquad (4)$$

where $a = 2{\cdot}86 \times 10^{-8}$ cm. for α-iron. The mean time of stay τ' is related to the relaxation time τ by the expression [2, 7, 8]

$$\tau' = \frac{3}{2}\tau \qquad (5)$$

For a period of oscillation of 1·3 sec. the temperature of maximum damping is found to be 21·5° C. The relaxation time at this temperature is thus given by

$$\tau(21{\cdot}5^\circ\text{ C.}) = \frac{1}{\omega} = \frac{1{\cdot}3}{2\pi} = 0{\cdot}21 \text{ sec.}$$

From equations (5) and (4) it follows that

$$D(21{\cdot}5^\circ\text{ C.}) = 1{\cdot}1 \times 10^{-16} \text{ sq. cm./sec.}$$

For a period of oscillation of 5·7 sec. the temperature of maximum damping proved to be 9·5° C., giving

$$D(9{\cdot}5^\circ\text{ C.}) = 2{\cdot}5 \times 10^{-17} \text{ sq. cm./sec.}$$

The temperatures of maximum damping were derived from Fig. 1*a*, which shows the internal friction peaks of an iron wire containing about 0·1 at.-% of nitrogen for periods of oscillation of 1·3 and 5·7 sec. After correction for background damping the peak heights are exactly proportional to the reciprocal of absolute temperature. This was anticipated in Polder's theory,[2] according to which Δ (*see* equation (3)) is inversely proportional to T. Strictly speaking, therefore, the maximum of the internal friction peak is not found where $\omega\tau = 1$, but where $\omega\tau/T(1 + \omega^2\tau^2)$ has its maximum value, or, according to equation (1), where $U/RT = (\omega^2\tau^2 + 1)/(\omega^2\tau^2 - 1)$. Application of this formula gives only small corrections to the values as calculated above. With $U =$ 18,600 cal./g. atom (*see* next section), the diffusion coefficients at 21·5° and 9·5° C. become $1{\cdot}1 \times 10^{-16}$ and $2{\cdot}4 \times 10^{-17}$ sq. cm./sec., respectively.

DIFFUSION COEFFICIENTS AT 500°, 600°, AND 950° C.

The diffusion coefficient at a high temperature can be determined from measurements of the rate of

Table I
VALUES OF *D* FOR NITROGEN IN IRON

Temp., ° C.	*D* Experimental, sq. cm./sec.	*D* Calculated from Equation (12), sq. cm./sec.
9·5	$2{\cdot}4 \times 10^{-17}$	$2{\cdot}7 \times 10^{-17}$
21·5	$1{\cdot}1 \times 10^{-16}$	$1{\cdot}0 \times 10^{-16}$
500	$3{\cdot}8 \times 10^{-8}$	$3{\cdot}6 \times 10^{-8}$
600	$1{\cdot}4 \times 10^{-7}$	$1{\cdot}4 \times 10^{-7}$
950 (α)	——	$3{\cdot}1 \times 10^{-6}$
950 (γ)	$6{\cdot}5 \times 10^{-8}$	——

absorption or desorption of nitrogen by an iron wire if diffusion in the metal is rate-determining, *i.e.*, if diffusion is much slower than the surface reaction.[9] When a cylindrical wire with a uniform concentration c_a of the gas has been held for a time t at a temperature for which the diffusion coefficient of the gas in the metal is D, and in such a gas atmosphere that the final equilibrium concentration at $t = \infty$ would be c_e, the mean concentration of gas $\bar{c}$ in the metal is given as a function of t by

$$\frac{\bar{c}-c_e}{c_a-c_e} = \sum_{v=1}^{v=\infty} \frac{4}{\xi_v^2}\, e^{-\xi_v^2 Dt/R^2} \quad \ldots\ldots\ldots\ldots (6)$$

Here the values of ξ_v are the roots of the equation $J_0(x) = 0$, where $J_0(x)$ is the Bessel function of zero order ($\xi_v = 2{\cdot}405,\ 5{\cdot}520,\ 8{\cdot}654,\ 11{\cdot}792,\ \ldots.$), and R is the radius of the wire.

Equation (6) applies to both $c_a > c_e$ and $c_e > c_a$, *i.e.*, to both desorption and absorption of gas. For large values of t the sum in equation (6) can be replaced in a good approximation by its first term :

$$\log \frac{\bar{c}-c_e}{c_a-c_e} \cong -0{\cdot}160 - 0{\cdot}4343\ \frac{t}{\tau''} \quad \ldots\ldots\ldots (7)$$

where

$$\tau'' = \frac{R^2}{5{\cdot}784\ D} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Equation (7) gives satisfactory results for $t > \tau''/3$, or, in other words, for

$$\log \frac{\bar{c}-c_e}{c_a-c_e} < -0{\cdot}3 \quad \ldots\ldots\ldots\ldots\ldots (9)$$

If diffusion is indeed rate-determining, then, according to equations (7) and (9), a straight line will be obtained by plotting values of $\log (\bar{c}-c_e)/(c_a-c_e) < -0{\cdot}3$ against time. This straight line and the ordinate axis will intersect at point (0, −0·16). If, on the other hand, the reaction at the gas/metal interface is rate-determining, no straight line satisfying this condition will be obtained. In the first case (diffusion rate-determining) τ'' is given by the slope of the straight line (eq. (7)) and D is given by eq. (8).

In the authors' experiments iron wires were loaded with nitrogen at 950° C. by heating them in 99 vol.-% N_2 + 1 vol.-% H_2. Desorption took place by heating for varying periods at 500°, 600°, or 950° C. in a stream of wet hydrogen.* After its pre-selected period of heating, each wire was quenched in water. In that condition the height of the internal friction peak is not a direct measure of the nitrogen content ; the peak is too low, because the outer zone of the wire contains less nitrogen per unit of volume than its interior. The wires were homogenized by heating them for 1 hr. at 560° C. in pure nitrogen. Separate experiments showed that no absorption or desorption of nitrogen takes place during this treatment. The peak height $Q_{\max}^{-1}(t)$ after quenching from 560° C. in water is a direct measure of the residual nitrogen content (*see* Fig. 1*b*).

As the final equilibrium concentration c_e is zero in the desorption experiments, and as the peak height is proportional to the uniform concentration, equation (7) reduces to

$$\log \frac{Q_{\max}^{-1}(t)}{Q_{\max}^{-1}(t=0)} \cong -0{\cdot}160 - 0{\cdot}4343\ \frac{t}{\tau''} \quad \ldots\ldots\ldots (10)$$

when

$$\log \frac{Q_{\max}^{-1}(t)}{Q_{\max}^{-1}(t=0)} < -0{\cdot}3 \quad \ldots\ldots\ldots\ldots (11)$$

Figures 2*a* and *b*, relating to temperatures of 500° and 600° C., respectively, show that plots of $\log [Q_{\max}^{-1}(t)/Q_{\max}^{-1}(t=0)]$ against time give straight lines through point (0, −0·16), indicating that at the temperatures mentioned diffusion is rate-determining in the desorption of nitrogen in an atmosphere of hydrogen.† Each point in Figs. 2*a* and *b* relates to a separate wire. Table I gives the values of D derived from Fig. 2 with the aid of equations (8) and (10). The value of D for 950° C. was determined in the same way and was found to lie between the values for 500° and 600° C. For completeness, the values of D for 9·5° and 21·5° C. are also included in the Table.

In Fig. 3 $\log D$ is plotted against the reciprocal of the absolute temperature. The values for α-iron lie on a straight line‡ which yields the following equation for the dependence of D on absolute temperature :

$$D_N(\alpha) = 6{\cdot}6 \times 10^{-3}\, e^{-18{,}600/RT} \text{ sq. cm./sec.} \quad \ldots\ldots (12)$$

The values $D_0 = 6{\cdot}6 \times 10^{-3}$ sq. cm./sec. and $U =$ 18,600 cal./g. atom for α-iron are to be compared with those of Wert,[10] *i.e.*, $D_0 = 3 \times 10^{-3}$ sq. cm./sec. and $U = 18{,}200$ cal., derived from measurements over a much smaller range of temperature.

*Separate experiments indicated that dry hydrogen gives identical results if the hydrogen used is free of carbon compounds.

†This is not the case for the absorption of nitrogen, as will be shown in a future paper.

‡The experiments at 9·5° and 21·5° C. seem to indicate that in the low-temperature region U is greater than its mean value in the whole region (18,600 cal./g. atom), so that probably the line is slightly curved upwards.

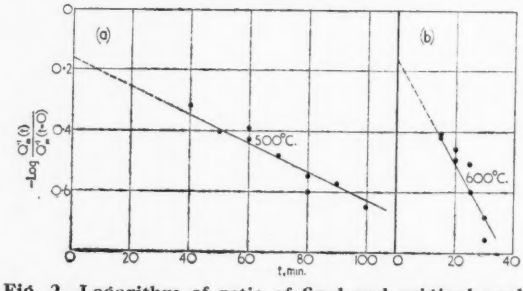

Fig. 2—Logarithm of ratio of final and original peak heights for various times of desorption in an atmosphere of hydrogen at (*a*) 500° C. and (*b*) 600° C. Each point corresponds to a separate wire

The value of D_N at about 950° C. for γ-iron was determined roughly by Darken, Smith, and Filer,[11] yielding a value three times larger than the present authors' value given in Table I. The diffusion coefficient at 1348° C. was determined more accurately by these authors. Their values are :

$$D(955°,\gamma) = 1{\cdot}9 \times 10^{-7} \text{ sq. cm./sec.}$$
$$D(1348°,\gamma) = 3{\cdot}1 \times 10^{-6} \text{ sq. cm./sec.}$$

DISCUSSION

A remarkable fact revealed by the measurements is that the diffusion coefficient of nitrogen in α-iron is much greater than that in γ-iron. At 540° C. the diffusion coefficient of nitrogen in α-iron has already surpassed the 950° C. value of D in γ-iron. At 950° C. the extrapolated value of α-iron is about 50 times that for γ-iron. Analogous phenomena were found for interstitial diffusion of carbon and hydrogen in iron.

The first to observe a difference in the diffusion coefficients of interstitial solute atoms in α- and γ-iron was Snoek,[12] when experimenting with iron samples containing carbon. The best expression for the diffusion coefficient of carbon in α-iron was derived by Wert[8] by combining his own measurements on elastic after-effect and internal friction with those on diffusion carried out by Stanley[13] at higher temperatures :

$$D_C(\alpha) = 2 \times 10^{-2} e^{-20{,}100/RT} \text{ sq. cm./sec.} \quad \ldots (13)$$

The best expression for the diffusion coefficient of carbon in γ-iron is perhaps that of Wells and Mehl[14] :

$$D_C(\gamma) = 7 \times 10^{-2} e^{-32{,}000/RT} \text{ sq. cm./sec.} \quad \ldots (14)$$

Corresponding equations for the diffusion coefficients of hydrogen in α- and γ-iron were calculated by Sykes, Burton, and Gegg[15] from published values of the solubility of hydrogen in iron and of the rate of permeation of hydrogen through iron walls. A critical re-examination of the available data on solubility and permeability led Geller and Sun[16] to the following equations, slightly different from those of Sykes and his collaborators :

$$D_H(\alpha) = 2{\cdot}2 \times 10^{-3} e^{-2900/RT} \text{ sq. cm./sec.} \ldots (15)$$
$$D_H(\gamma) = 1{\cdot}1 \times 10^{-2} e^{-9950/RT} \text{ sq. cm./sec.} \quad \ldots (16)$$

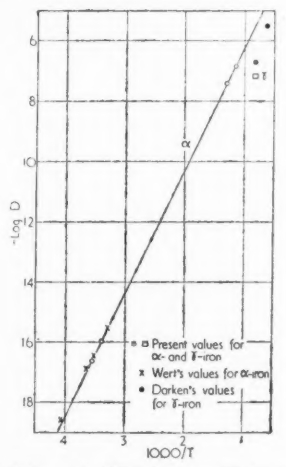

Fig. 3—Logarithm of diffusion coefficient of nitrogen in α-iron plotted against $1/T$

Table II

VALUES OF D AT VARIOUS TEMPERATURES AND OF $D(\alpha)/D(\gamma)$ AT 950° C.

Temp., ° C.	D Hydrogen, sq. cm./sec.	D Nitrogen, sq. cm./sec.	D Carbon, sq. cm./sec.
20	$1{\cdot}5 \times 10^{-5}$	$8{\cdot}8 \times 10^{-17}$	$2{\cdot}0 \times 10^{-17}$
100	$4{\cdot}4 \times 10^{-5}$	$8{\cdot}3 \times 10^{-14}$	$3{\cdot}3 \times 10^{-14}$
300	$1{\cdot}7 \times 10^{-4}$	$5{\cdot}3 \times 10^{-10}$	$4{\cdot}3 \times 10^{-10}$
500	$3{\cdot}3 \times 10^{-4}$	$3{\cdot}6 \times 10^{-8}$	$4{\cdot}1 \times 10^{-8}$
700	$4{\cdot}9 \times 10^{-4}$	$4{\cdot}4 \times 10^{-7}$	$6{\cdot}1 \times 10^{-7}$
900	$6{\cdot}3 \times 10^{-4}$	$2{\cdot}3 \times 10^{-6}$	$3{\cdot}6 \times 10^{-6}$
950 (α)	$6{\cdot}7 \times 10^{-4}$	$3{\cdot}1 \times 10^{-6}$	$5{\cdot}1 \times 10^{-6}$
950 (γ)	$1{\cdot}8 \times 10^{-4}$	$6{\cdot}5 \times 10^{-8}$	$1{\cdot}3 \times 10^{-7}$
$\frac{D950\ (\alpha)}{D950\ (\gamma)}$	~ 4	~ 50	~ 40

Table II gives the values of diffusion coefficients of nitrogen, carbon, and hydrogen in α-iron at 20°, 100°, 300°, 500°, 700°, 900°, and 950° C. as derived from equations (12), (13), and (15), respectively, and at 950° C. for γ-iron as given by Table I for nitrogen and as derived from equations (14) and (16) for carbon and hydrogen. The ratios $D(\alpha)/D(\gamma)$ at 950° C. are also included in Table II.

Most important is the fact, revealed by Fig. 3 and Table I, that the values of D_N at 9·5° and 21·5° C., as calculated from the authors' internal friction measurements, correspond well with the values at these temperatures obtained by extrapolation from the region 500–600° C., where conventional diffusion experiments were carried out. This forms a strong support for the correctness of the interpretation of damping caused by carbon and nitrogen as given by Snoek[1] and Polder.[2] Similar support is derived from the combined measurements of Stanley[13] and Wert.[8]

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Letter to the Editor

EFFECT OF PLASTIC DEFORMATION ON CARBIDE PRECIPITATION IN STEELS

Cottrell[1, 2] has shown that a consideration of the interaction between carbon atoms and edge dislocations in iron leads to the prediction that the energy binding a carbon atom in a dislocation is greater than that binding it in an iron-carbide particle. Until now, experimental evidence quoted in support of this prediction[2,3] has related to low-carbon steels. Hundy[4] has recently raised the question of the extent to which precipitation of carbide from solution may be prevented by plastic deformation. Observations I have made on higher-carbon materials suggest that the effect can be surprisingly large.

Figure 1 relates to a 0·7% C plain-carbon steel which was water-quenched from 800° C. and then locally deformed, on a surface free from decarburization, using a pyramidal indenter. After indentation the specimen was tempered at 200° C. for 2 hr.; the surface was then polished down to about half the depth of the indentation and was finally etched in 5% picral. Electron-microscopical examination of similar specimens gave evidence of carbide precipitation in the undeformed dark-etching regions, but no evidence of precipitation was found in the light-etching regions affected by plastic deformation; the latter showed an etching behaviour essentially similar to that of untempered martensite. Prolonged tempering at about 200° C. was required to induce visible precipitation within the deformed regions. Figures 2*a* and *b* relate to an 0·45% carbon steel which was indented after quenching and then tempered at 200–220° C. for 25 days. After this period the carbide particles had grown sufficiently to allow recognition using a light microscope. Evidently precipitation was appreciably less within the deformed region.

These effects have been observed in a variety of plain-carbon and alloy steels which form martensite on quenching. In plain-carbon steels some evidence of precipitation was found in the deformed regions after a short period of tempering at a temperature above about 250° C., but even after 2 hr. at 350° C. the deformed regions etched to an appreciably lighter shade than that of the surrounding material. During tempering at temperatures above about 450° C., however, the differences in etching properties decreased rapidly until, generally, no distinction could be made by ordinary etching techniques.

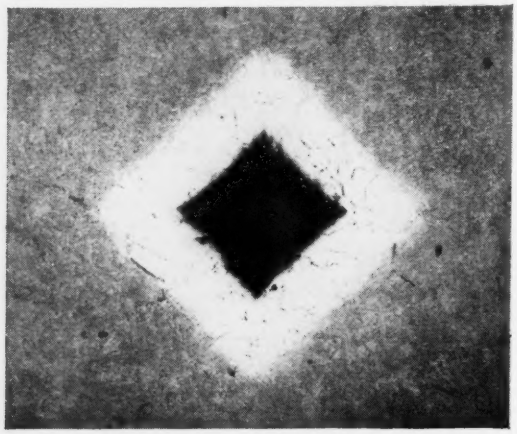

Fig. 1—Plain-carbon steel (0·7% C) W.Q. from 800° C., locally deformed, and tempered at 200° C. for 2 hr. × 120

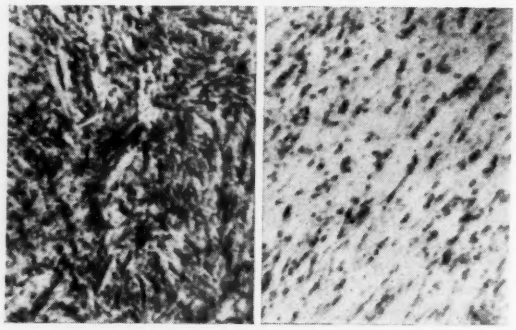

Fig. 2—0·45% carbon steel W.Q., indented, and tempered at 200–220° C. for 25 days: (*a*) Undeformed region; (*b*) deformed region. Etched in 5% picral × 2500

It appears that a similar method of local deformation can be applied to give evidence of carbide 'solution' in steels containing precipitated carbides. In this case, so far as may be judged from the 'light-etching' effects developed, in medium- or high-carbon steels the amount of carbide which may be taken into 'solution' in the deformed regions, even when subsequent ageing is carried out at an elevated temperature, is very much less than that which is retained in 'solution' when deformation is applied before precipitation.

The condition and particle size of the carbide appear to be important. In the case of a 0·7% carbon steel, clear etching differences were observed with specimens indented after a low-temperature tempering which would precipitate the ε iron carbide. Less marked effects were obtained with specimens tempered at 300–350° C. and if the tempering which preceded deformation was carried out at a temperature above 400–450° C. no recognizable difference in etching properties between the deformed and the undeformed regions was developed.

One possibility suggested by these observations is that the density of dislocations, or other lattice imperfections with which carbon atoms can become associated, depends appreciably on the microstructure of the steel as well as on the amount of deformation applied.

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Mercury-Cathode Electrolysis and Its Application to Steel Analysis

By the Methods of Analysis Committee

SYNOPSIS

A method is described for mercury-cathode electrolysis applicable over a wide range of alloy compositions, which gives optimum conditions for removal for large amounts of cathodically deposited elements, *e.g.*, iron, chromium, and nickel.

Experimental evidence shows that after electrolysis the solution can be used for the quantitative determination of various trace elements, *e.g.*, aluminium, titanium, vanadium, and zirconium.

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THE separation of metals by mercury-cathode electrolysis has been practised for many years, but its application has mainly been limited to the removal of relatively small amounts of metal. The operation is time-consuming, because deposition is slow with the conventional type of cell. Where appreciable amounts of metal are to be removed, it is usual to apply electrolysis merely as a secondary or refining stage after preliminary separation of most of the iron by ether extraction or bicarbonate hydrolysis.

The purpose of the present investigation was to develop conditions for the direct application of mercury-cathode electrolysis as a primary separation for large weights of steel, *e.g.*, 10 g. If suitable conditions could be derived, a number of potential applications would arise, *e.g.*, the determination of small amounts of aluminium, vanadium, titanium, and zirconium in high-chromium and other alloy steels where the solutions are too complex for the direct application of orthodox procedures.

The investigation has been conducted by the Highly Alloyed Steels and Ferro-Alloys Analysis Sub-Committee.* Most of the experimental work has been carried out by a small study group appointed by the Sub-Committee and consisting of Mr. B. Bagshawe (convenor), Mr. E. Dyke, Mr. L. E. Gardner, Mr. C. L. Grayson, and Mr. J. D. Hill.

THE CELL ASSEMBLY

The proposed mercury-cathode cell assembly is shown in Fig. 1. It consists of a 1000-ml. squat resistance-glass beaker containing 150 ml. (approx. 2000 g.) of pure clean mercury. The mercury-cathode surface area is approx. 85 sq. cm., giving a current density of 0·175 at 15 amp.

The electrical connection to the mercury is made by means of a stout copper or nickel wire (10 S.W.G.) sheathed in a glass tube, and fixed in position before introducing the electrolyte. The anode shown in Fig. 1 is prepared from platinum tape (1·25 cm. wide) wound round the cooling coil. Various other types of anode have been used, including circular perforated platinum discs, flat rings of 3 in. overall dia. with $\frac{3}{4}$ in. dia. centre cut out, flat wire spirals, and gauze circles. These types are best situated below the cooling coil, which then has the additional function of reducing anodic spray. Experience to date points very definitely to the view that anodes should be of large surface area and should be placed, so far as possible, in the horizontal plane. The anode is situated about 2·5 cm. above the cathodic surface.

A water-cooling coil is a necessary part of the assembly, as a means of maintaining the electrolyte at optimum temperature. The heat developed by electrolysis at high current densities is such that without some means of temperature control the solution would rapidly reach boiling point. The cooling system is a flat spiral of $\frac{3}{16}$-in. internal dia. glass tubing situated internally. This spiral, if separate from the anode, should be situated about 4–5 cm. above the mercury surface, and the flow of water should be capable of maintaining the electrolyte at less than 40° C.

The mercury is stirred by a motor-operated glass paddle with blades below the cathode surface. The design of the paddle in relation to the speed has been shown to be critical. The paddle should have straight blades, because spiral or twist blades produce an uneven disturbance of the mercury which, at high rotation speeds, may cause an electrical short-circuit by the projection of mercury droplets on to the anode surface. A straight two-bladed paddle with blades 3·5 cm. long × 1 cm. deep is suitable. A speed of about 300 r.p.m. has been found to be satisfactory; the danger of excessive speeds is stressed, as in such

* The composition of the Sub-Committee was: Mr. B. BAGSHAWE (*Chairman*), Brown-Firth Research Laboratories; Mr. C. D. ATKINSON, Sheffield Testing Works Ltd.; Dr. J. CAMERON (to 31.3.50), Clyde Alloy Steel Co., Ltd.; Mr. E. DYKE (to 31.3.52), Brown-Firth Research Laboratories; Mr. W. T. ELWELL (to 31.3.52), Imperial Chemical Industries; Mr. J. W. FLINT, Wm. Jessop and Sons Ltd.; Mr. L. E. GARDNER, Edgar Allen and Co., Ltd.; Mr. C. L. GRAYSON, English Steel Corporation Ltd.; Mr. E. W. HARPHAM, Richard Thomas and Baldwins Ltd.; Mr. S. HARRISON, Kayser, Ellison and Co., Ltd.; Mr. J. D. HILL, Bragg Laboratory, N.O.I.D.; Mr. G. M. HOLMES, London and Scandinavian Metallurgical Co.; Mr. G. MURFITT (to 31.3.49), Metals and Methods Ltd.; Mr. R. T. POSTLETHWAITE, Samuel Fox and Co., Ltd.; Mr. L. N. TAYLOR, Samuel Osborn and Co., Ltd.; and Mr. J. L. WEST, Hadfields Ltd.

Paper MG/D/114/53 of the Methods of Analysis Committee of the Metallurgy Division of the British Iron and Steel Research Association, received 15th July, 1953.

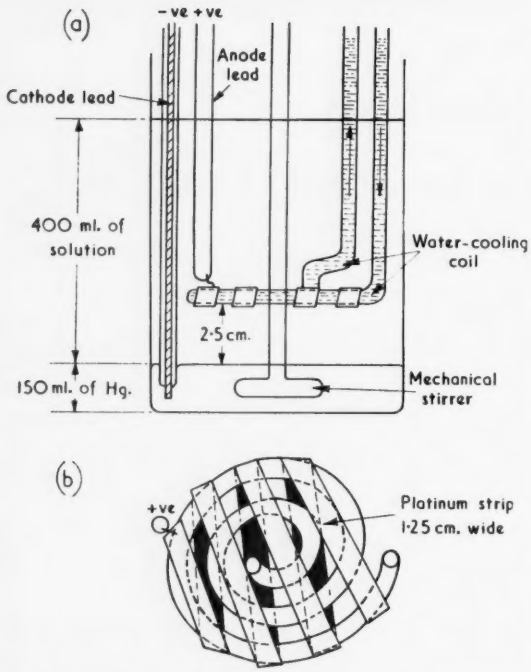


Fig. 1—(*a*) Mercury-cathode assembly; (*b*) plan of anode and cooling coil

cases a vortex is produced in the mercury which may be sufficient to cause the electrolyte to make contact with the copper-wire cathode connection.

The importance of stirring the mercury is emphasized because most of the literature references regard stirring as unnecessary or even detrimental; where it is advocated it is often achieved by simply bubbling a stream of air through the electrolyte. Experiments with a static cathode have been entirely unsatisfactory. The amount of amalgam formation is so great in 10-g. depositions that the cathode efficiency deteriorates rapidly unless a fresh surface is exposed to the electrolyte by constant stirring during the whole of the deposition period. The relative inefficiency of non-stirred tests is shown clearly in the results of the first deposition trials (Table I).

The D.C. supply to the cell, in circuit with a suitable variable resistance, should be in the range 10–20 amp.

The apparatus described is put forward tentatively as a means of establishing a design for a permanent equipment. It is readily constructed from ordinary laboratory equipment and has proved generally successful in operation. On the other hand it is cumbersome, and it is hoped that an apparatus combining good design with maximum efficiency and convenience of operation will be forthcoming from laboratory-instrument manufacturers.

DEPOSITION TRIALS

For the purpose of preliminary trials two steels were selected:

MC1 Plain-carbon steel (0·67% Mn, 0·07% Cr)
MC2 Stainless steel (0·2% Mn, 10·7% Cr)

Samples of these steels weighing 10 g. were decomposed with 120 ml. of sulphuric acid (1 : 9) and filtered, and the residue was returned to the main solution after removal of the silica with hydrofluoric acid, fusion of the residue with 5 g. of potassium bisulphate, and extraction with 100 ml. of sulphuric acid (1 : 99). The free acidity at the start of electrolysis was equivalent to about 4 ml. of sulphuric acid (sp. gr. 1·84) in a volume of 400 ml. Electrolysis was carried out at current densities varying from 0·117 to 0·234 amp./sq. cm. for varying periods and the final electrolytes were analysed for residual iron, chromium, and manganese. The results are summarized in Table I.

The figures shown for the plain-carbon steel MC1 indicate that for an electrolysis period of 2–2½ hr. at 10 amp. (0·117 amp./sq. cm.) deposition of iron and manganese is almost quantitative and only traces of each remain in the electrolyte. At 20 amp. the deposition rate is proportionately increased, *i.e.*, deposition is virtually complete in 1 hr. The chromium steel MC2 gave a much more erratic performance and in certain instances complete failure to deposit chromium was noted.

Extended trials on these two steels have been conducted using various modifications of these preliminary test conditions, and the following broad observations were made.

Current/Cathode Surface Area

This is the most important single feature affecting the efficiency of deposition. The rate of metal deposition in the mercury, other conditions being fixed, is approximately proportional to the applied current in relation to the area of mercury-cathode surface. A large cathode surface is necessary for rapid deposition of large amounts of iron, chromium, etc., and the applied current must be high enough to give a current density of preferably not less than 0·17 amp./sq. cm. Mercury in a 1000-ml. squat beaker gives a cathode surface of about 85 sq. cm., and a current of 15 amp. is necessary to give this current density.

At lower current densities deposition rates are reduced and other troubles arise, in particular deposition of manganese at the anode. High current densities are advantageous in promoting increased deposition rate, but practical difficulties arise at very high currents (over 20 amp.); *e.g.*, arcing, excessive spray loss, and difficulty in maintaining efficient cooling of the electrolyte.

Cell Voltage

The potential difference across the cell drops progressively during deposition, *e.g.*, from about 15 to 7 V., with a corresponding rise of cell current towards the end of effective electrolysis. The ideal condition would be to regulate cell voltage during deposition so as to maintain the starting potential, but this would necessitate very high currents towards the end of electrolysis. The best compromise is to regulate the rising current to a maximum of 15 amp. during the initial stage of the electrolysis, and subsequently to allow the normal rise of cell current to occur without further regulation, so as to facilitate chromium deposition.

Temperature of Electrolyte

For practical reasons some control of temperature is necessary with an electrolysis current of 15–20 amp. Also, the increasing potential difference across the cell with rising temperature reduces the efficiency of chromium deposition; to maintain optimum electrolysis conditions for high chromium concentrations it would be necessary to increase the current. Furthermore, a high electrolyte temperature seems to favour the formation of a black chromium-rich deposit. A cooling device to maintain the electrolyte temperature below 40° C. is therefore recommended.

Distance between Electrodes

With 400 ml. of solution in the cell, the maximum spacing possible when the anode is situated just below the liquid surface is about 5 cm. Tests at 5-cm. and 2·5-cm. spacings have shown no marked difference (Table II), but spraying above the liquid surface is more severe at maximum spacing. It is not advisable to reduce the spacing much below 2·5 cm. owing to the risk of arcing at high currents.

FREE ACIDITY

Maximum deposition rate of iron, chromium, etc., is obtained with a minimum acidity in the initial electrolyte. This feature is important in relation to the efficient deposition of large amounts of metal, since the sulphate equivalent of all deposited metals is released during deposition and exists as free acid in the final solution. Thus, 10 g. of iron as ferrous sulphate releases the equivalent of 9·5 ml. of sulphuric acid (sp. gr. 1·84) during its deposition, and chromium releases the equivalent of 1·54 ml. per g. of metal.

It is therefore of advantage to electrolyse ferrous sulphate solutions, rather than oxidized solutions containing iron as the ferric salt, which releases an increased equivalent of sulphuric acid.

The minimum volume of sulphuric acid (1 : 9) required to dissolve 10 g. of steel is 100 ml. This provides only a small excess of free acid. As, however, different supplies of concentrated acid show significant variations when made up to nominal 1 : 9 strength (*e.g.*, two preparations of 1 : 9 acid gave specific gravities of 1·10 and 1·11, respectively) acid corrected to sp.gr. 1·11 has been used in the experimental work.

It was found undesirable to restrict the starting acid to the theoretical minimum because in this case there is definite danger of hydrolysis during the early stages of electrolysis. Furthermore, it would be necessary to calculate the theoretical acid requirement depending on the iron/chromium ratio, *e.g.*, 10 g. of iron = 100 ml. of sulphuric acid (sp. gr. 1·11), 10 g. of chromium = 160 ml. of the same acid. Finally, solution of the steel is unnecessarily prolonged unless an appreciable excess of free acid is present.

Table II

TESTS WITH DIFFERENT ANODE/CATHODE SPACINGS

Steel MC2; electrolysis for 3 hr.

Anode/Cathode Spacing, cm.	Amounts in Residual Electrolyte, mg.		
	Fe	Mn	Cr
2·5	1·4	1·1	0·9
	6·4	1·4	2·6
5·0	6·8	1·3	4·9
	2·4	0·8	1·2

Table I

RESULTS OF FIRST DEPOSITION TRIALS

Operator	Current, amp.	Temp., °C.	Time, hr.	Residual Elements after Electrolysis, mg.		
				Fe	Cr	Mn
Steel MC1						
1	10	36	2·5	7	nil	11
	,,	34	2·5	770	...	15 (not stirred)
	15	39	2·5	7	nil	4
	,,	36	2·5	14	nil	4 (not stirred)
	20	43	1·0	12	nil	5
	,,	54	1·0	21	nil	3 (not stirred)
	10	26	2·5	60	...	4 (extremely vigorous stirring)
2	17	25	2·0	16	...	3
3	10	70	2·5	400	...	12 (not stirred)
	10	70	3·0	4	...	3
4	15	70–80	3·5	15	0·8	17 (not stirred)
Steel MC2						
1	10	40–50	2·5	(deposition unsatisfactory)		
	15	40–50	2·5	,,	,,	
	20	40–50	2·0	7	9	1·2
	15	40–50	2·5	nil	2	1 (electrolysed at 500 ml. vol. and diluted to 600 ml. at constant p.d.)
2	17	25	3·0	4·7	14	1·4
3	No satisfactory depositions obtained					
4	15	70–80	4·0	1·4	5·2	7·8 (without stirring)

Table III

EFFECT OF VARYING ACIDITY ON DEPOSITION RATES

Steel	Solvent Acid, ml. of H_2SO_4 (sp.gr. 1·11)	Amounts in Residual Electrolyte after 3 hr. at 16 amp.		
		Fe	Mn	Cr
MC2 (10·7% Cr)	100	2·5	0·9	nil
,, ,, ,,	120	3·6	1·1	2·0
		Electrolysis Time at 15 amp.*		
		Hr.		Min.
MC3 (plain steel)	105	1		45
,, ,, ,,	165	2		0
MC3 (4 g.)+Cr metal (6 g.)	140	3		30
,, ,, ,, ,,	165	4		0

* These times refer to tests run to limiting 5-mg. amounts of Fe, Mn, and Cr

A higher acid concentration may be used to facilitate solution of the steel, and the optimum acidity of the electrolyte can then be attained by the addition of sodium carbonate. Such neutralization should always be made before the start of electrolysis. Neutralization during electrolysis is not recommended; when this has been done, unsatisfactory results have been obtained owing to local hydrolysis. If a high enough current density is maintained throughout, it is not necessary to neutralize the acid released during the electrolysis, because the increased acidity does not unduly prolong the electrolysis time.

Thus 10 g. of carbon steel dissolved in 165 ml. of sulphuric acid (sp. gr. 1·11) takes 2 hr. to electrolyse, compared with $1\frac{3}{4}$ hr. when the steel is dissolved in 105 ml. of the same acid (*see* Table III). This indicates that it is not necessary to use acid of a precise concentration, and so dilute acid (1 : 9) is specified in the procedure.

EFFECT OF ALKALI SALTS

It has previously been mentioned that in cases where excess sulphuric acid is used to dissolve the steel, an optimum starting acidity for electrolysis can be obtained by making calculated additions of sodium carbonate. Sodium hydroxide may also be used, but the carbonate is preferred. There is no interference from the sodium ion introduced, and if the addition of alkali produces a turbidity it may be due to local precipitation arising from too rapid neutralization. In such cases, a clear solution may be obtained by heating to 60° C., followed by cooling before electrolysis.

The non-interference of sodium salts suggests that insoluble siliceous or carbide-bearing residues may be decomposed separately by sodium carbonate fusion and returned to the mother liquor after aqueous extraction and acidification. Tests in which the equivalent of 50 mg. of chromium has been fused with 5 g. of sodium carbonate and added to the electrolysis solution in this way have shown no adverse effects (Table IV). Subsequent tests on actual steel samples have not, however, always been so successful, and in several instances where the acid-insoluble carbide residues from complex alloy steels have been recovered by alkali carbonate fusion the electrolysis has been adversely affected, deposition ceasing at an incomplete stage or being considerably prolonged.

Ammonium salts cause interference, particularly when chromium is present, and are best avoided (Table IV).

EFFECT OF CERTAIN METALS

Manganese

Anodic deposition of manganese dioxide has several times been noted. The evidence suggests that such deposition is related to the current density; except at very high manganese concentrations, no difficulty is encountered with a current of 15–20 amp. At 10 amp. substantial anodic deposition occurred in certain instances, even from 0·2% manganese steel. It seems to take place in the later stages of electrolysis, *i.e.*, after deposition of the iron, and its effect may be to reduce the anode surface efficiency and thus retard

Table IV

EFFECT OF ALKALI ADDITIONS

Steel MC2: Electrolysis for 3 hr. at 16 amp.

Solvent Acid, ml. of H_2SO_4 (sp.gr. 1·11)	Alkali Addition	Amounts in Residual Electrolyte, mg.		
		Fe	Mn	Cr
100	...	2·5	0·9	nil
200	70 ml. NaOH (20%)	7·6	1·1	3·2
150	35 ,, ,, ,,	5·3	0·9	1·1
150	40 ,, NH_4OH (1 : 3)	11·2	0·8	12·2*
110	...	6·7	0·8	1·0
150	7·5 g. Na_2CO_3	7·0	0·6	1·0
110	50 mg. of Cr as $K_2Cr_2O_7$ solution added to electrolyte	7·0	0·8	3·5
110	50 mg. of Cr added to electrolyte after fusion with 5 g. of Na_2CO_3 and neutralization of extract	...	0·6	3·1

* This test showed the black chromiferous deposit

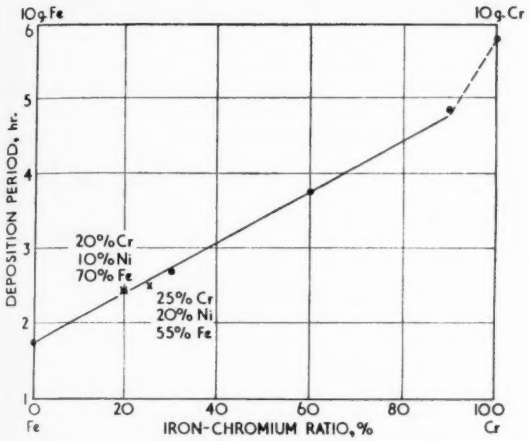


Fig. 2—Deposition efficiency for iron–chromium series

the later stages of chromium deposition. No serious effect has been noted in 10-g. tests containing the equivalent of 1·7% of manganese (Table V), but with steels containing 10–14% of manganese there is very heavy anodic deposition and much manganese remains in the electrolyte. This difficulty can, however, be overcome by using a smaller sample weight.

Chromium

Chromium is definitely the most difficult metal to deposit. The deposition rate is much slower than the corresponding rate for iron, but the best conditions developed to date have shown a marked advance in the efficiency of chromium deposition and it is now possible to deposit the chromium from 10 g. of chromium metal in 5–6 hr. (Fig. 2). Chromium amalgam appears to be comparatively unstable and the earlier work has shown several examples where electrolysis has been retarded or stopped altogether by the formation of a black chromium-bearing residue. This effect of chromium has been reported by other investigators, but its precise nature and cause do not appear to be well defined. Earlier work suggests that there is a greater tendency to form ' chromium black ' when chromium residues are fused with an alkali metal carbonate or bisulphate before introduction to the main electrolyte, but the evidence is not decisive. There is considerably more support for the opinion that ammonium salts enhance the tendency to form these black deposits. The purity of the mercury may also

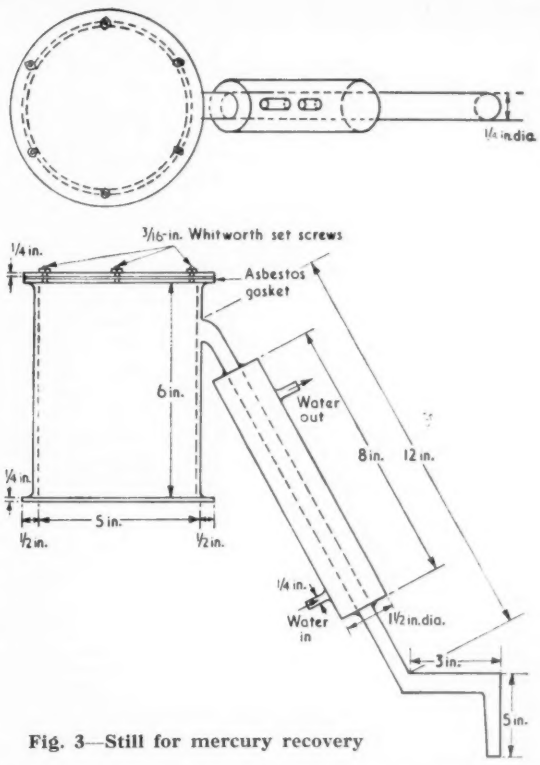


Fig. 3—Still for mercury recovery

play an important part, as it has often been noted when impure mercury or mercury not properly freed from amalgam has been used. A too finely adjusted free acidity may be a factor, and neutralization during electrolysis should be avoided. Appreciation of these points has reduced this factor to negligible proportions in recent tests.

Molybdenum

Molybdenum concentrations exceeding about 50 mg. (equivalent to 0·5% on 10-g. basis) appear to have a considerable retarding effect on the removal of chromium. At some intermediate stage in the electrolysis, the formation of a lower-valency compound results in the production of a brown solution. This brown coloration eventually disappears, but the removal of chromium after this stage is very slow. Electrolysis of 10 g. of an 18% Cr–8% Ni steel containing 1¼% of Mo was incomplete after 4½ hr. A

Table V

EFFECT OF MANGANESE ON DEPOSITION

	Current, amp.	Time		Amounts in Residual Electrolyte, mg.		
		Hr.	Min.	Fe	Mn	Cr
Steel MC2 (0·2% Mn)	10	3	30	7·0	1·1	6·0
,, ,, + 1·5% Mn	10	3	30	5·0	3·1	5·0
Steel MC2	15	2	30	5·0	nil	3·5
,, ,, + 1·5% Mn	15	2	30	5·0	1·9	3·5

synthetic 10% chromium steel solution was electrolysed satisfactorily within 2½ hr., but the addition of 3% of molybdenum retarded chromium removal so much that it was incomplete after 8 hr.

CLEANING OF MERCURY

The mercury used for electrolysis should be as pure as possible, and thorough cleaning after each deposition is essential. Various methods of dross extraction have been considered, *e.g.*, squeezing through chamois leather, distillation, dropping through a column of dilute nitric acid, and air agitation in contact with nitric acid or sulphuric acid and hydrogen peroxide. Squeezing through chamois leather, although effective, was discounted as a potential health hazard. Filtration by suction through a sintered glass funnel has also been used with a fair measure of success, and details of the procedure adopted in this type of cleaning are given in Appendix II. The residual amalgam from this treatment may be reserved until sufficient has accumulated and its mercury content recovered by distillation in an iron or mild-steel still of the type shown in Fig. 3.

The question of mercury cleaning is, however, a rather formidable auxiliary to cathode electrolysis, because quite large amounts of heavily contaminated mercury are involved, and a simple means of reducing the operation to a convenient routine level is really needed.

RECOVERY OF METALS FROM THE ELECTROLYTE

Before finally drawing up test conditions for mercury-cathode electrolysis it seemed desirable to establish proof that elements remaining in the electrolyte after electrolysis (*e.g.*, aluminium, titanium, zirconium, and vanadium) could be recovered quantitatively, as this is a necessary premise for the application of the method in analytical determinations.*

Accurate synthetic additions of these elements were made to solutions of steel, which were electrolysed under the stated conditions. After the completion of a normal period of electrolysis the electrolytes were analysed for the elements in question, using accepted chemical methods of determination. The results, given in Table VI, confirm that in all cases the element is quantitatively retained in the electrolyte and may be recovered by a suitable procedure.

RECOMMENDED METHOD

Performance and Scope

The recommended method is described in Appendix I. Examples of steel types on which satisfactory results have been obtained include carbon steels, nickel steels containing up to 5% of nickel, low-alloy steels of the nickel–chromium, nickel–molybdenum, and nickel–chromium–molybdenum–vanadium types, stainless irons, and low-carbon austenitic steels which can be decomposed in dilute sulphuric acid.

The deposition efficiency for the iron–chromium series, varying from 100% iron to 100% chromium, is shown in Table VII and illustrated graphically in Fig. 2. Synthetic additions of nickel to simulate typical iron–chromium–nickel combinations introduce no complication. These results show a marked advance on previously accepted practice; 10-g. samples of plain and low alloyed steels can be electrolysed in 2 hr. and steels in the 20–30% chromium range in about 3 hr. In all cases the tests refer to electrolytes that have been run to a determined limiting value of less than 5 mg. each of the residual iron and chromium.

Limitations

The method has certain limitations, mainly related to specialized types of highly alloyed steels which are insoluble in dilute sulphuric acid or which yield large carbide residues that cannot be handled satisfactorily by the prescribed treatment. The difficulties noted in the application of the procedure are briefly summarized below. Since, however, these difficulties relate to a comparatively small number of highly specialized alloy types, they do not markedly affect the immediate value of the method in view of the very wide field of application which has already been established for its use.

(i) Solubility in dilute sulphuric acid is retarded by increasing nickel content. Whilst increasing chromium content tends to offset this effect, the practical solubility limit is reached at about 18% of chromium and 8% of nickel. The range may be extended greatly if the nature of the determination

Table VI

RECOVERY OF NON-ELECTROLYSED METALS AFTER ELECTROLYSIS

All additions made to mild steel MC1

	Operator	Equivalent Added, %	Equivalents Recovered from Electrolyte, %
Aluminium	A	0·198	0·203, 0·200
	B	0·020	0·019, 0·019$_5$, {0·019$_5$ / 0·018$_5$}
	C	0·50–	0·49–, 0·49–
	D	{0·199 / 0·020}	{0·198 / 0·020}
Titanium	A	0·20	0·201, 0·200
	B	0·050	0·051, 0·051
	C	0·50–	0·52–, 0·51–
	D	0·20–	0·186
Vanadium	A	0·288	0·288, 0·291
	B	0·050	0·051, 0·052, {0·051 / 0·052}
	C	0·50–	0·50–, 0·50–
	D	0·198	0·197
Zirconium	A	0·194	0·198, 0·198
	B	0·050	0·047, 0·049
	C	0·200	0·194
Calcium	A	0·201	0·202, 0·199
	B	0·050	0·049, 0·049
	C	0·50–	0·50–, 0·50–
	D	0·162	0·154
Magnesium	A	0·203	0·206, 0·205
	B	0·050	0·049, 0·052, 0·051
	C	0·50–	0·50, 0·50
	D	0·195	0·190

* For details of elements separated by mercury-cathode electrolysis *see* G. E. F. Lundell and J. I. Hoffman, " Outlines of Methods of Chemical Analysis," p. 94: 1938, New York, John Wiley and Sons, Inc.

permits the use of smaller sample weights, *e.g.*, 1–2 g. In addition to nickel, a high silicon content also impairs solubility. The importance of fine millings or drillings in difficult cases should be obvious.

The behaviour of low-carbon ferro-chromium samples is erratic, and hydrochloric acid has been used to prevent the material from becoming passive. Subsequent tests, however, indicated an adverse effect on the electrolysis time.

(ii) Steels which give rise to large insoluble carbide residues, such as the tungsten and tungsten–molybdenum high-speed tool steels, high-carbon chromium steels, and niobium steels, introduce difficulties. The bisulphate fusion treatment is not suitable for large carbide residues and, whilst alkali carbonate fusion is more successful, the subsequent separation of hydrolysis residues and the presence of complex chromium ions cause interference.

A further effect of large carbide residues is that the solution retains a higher initial acidity which is proportional to the amount of sample remaining unattacked. This reduces the rate of deposition.

Wet destruction of the carbide residue with a perchloric acid mixture appears to be the most promising line for further study. This, however, needs to be related to a full study of mercury-cathode electrolysis in perchloric acid solution, since if this technique could be adopted for steels the separate treatment of carbides would not arise.

APPENDIX I

Recommended Procedure for the Mercury-Cathode Separation

Apparatus

Set up the apparatus as described on p. 30; *see also* Fig. 1. Clean mercury must be used for each determination; details for the recovery of used mercury are given in Appendix II.

Solutions

Sulphuric-Acid Wash (1 : 99)—Add 10 ml. of sulphuric acid (sp.gr. 1·84) to about 700 ml. of water, cool, dilute to 1 litre, and mix.

Table VII

DEPOSITION RATES OF SYNTHETIC ALLOYS

10-g. tests electrolysed at 15 amp. to leave < 5 mg. of each element

Iron, g.	Chromium, g.	Nickel Added as $NiSO_4.xH_2O$, g.	Amount of Solvent Acid,* Sulphuric Acid (sp.gr. 1·11), ml.	Time	
				Hr.	Min.
10	nil	nil	105	1	45
8	2	,,	115	2	25
7	3	,,	120	2	40
4	6	,,	140	3	45
1	9	,,	160	4	50
nil	10	,,	165	5	45
7	2	1	105	2	25
5·5	2·5	2	100	2	30

Amounts calculated to give the same acidity at start of electrolysis

Ammonium Hydroxide (1 : 1)—Dilute 500 ml. of ammonium hydroxide (sp.gr. 0·880) to 1 litre.

Sodium Carbonate (15%)—Dissolve 15 g. of sodium carbonate (anhydrous) in water and dilute to 100 ml.

Sulphuric Acid (1 : 9)—Add 100 ml. of sulphuric acid (sp.gr. 1·84) to about 700 ml. of water, cool, dilute to 1 litre, and mix.

Procedure

Transfer 10 g. of sample to a 600-ml. squat beaker, add 160 ml. of 1 : 9 sulphuric acid (Note 1), and digest until action ceases and only a residue of carbides remains.

Filter through a pulp pad, and wash with hot 1 : 99 sulphuric-acid wash (Note 2). Collect the filtrate in a 600-ml. squat beaker.

To the filtrate add 50 ml. of sodium carbonate solution (15%), slowly and with constant stirring to ensure complete solution of any precipitate formed. Cool the solution and transfer to the electrolysis cell. Adjust the volume of the electrolyte to about 400 ml. and electrolyse under the conditions specified on p. 30, until an external spot test shows that the solution is free of iron (Note 3) or until the green colour of chromium sulphate is no longer visible (Note 4). Electrolyse for a further 15 min.

Switch off the stirrer motor and disconnect the current supply to the cell. Syphon the electrolyte into a 1000-ml. squat beaker and rinse the cell several times with water, combining the rinsings with the main solution. This operation should be carried out without undue delay. Filter the solution through a small pulp pad and wash with sulphuric-acid wash (1 : 99).

The solution is now ready for the determination of certain elements, *e.g.*, aluminium, vanadium, or titanium, by suitable methods of analysis.

Notes

(1) For smaller sample weights of steel use 12 ml. of sulphuric acid (1 : 9) for each 1 g. of sample plus 40 ml. excess. For ferro-chromium and chromium metal samples use 16 ml. of sulphuric acid (1 : 9) per 1 g. of sample plus 40 ml. excess.

(2) If the insoluble residue is likely to contain any portion of the element being determined, a recovery treatment may be applied as follows:

> Transfer the pad and residue to a platinum dish and ignite at a low temperature to remove carbonaceous matter. Cool, add 0·5 ml. of sulphuric acid (1 : 9), and 2 ml. of hydrofluoric acid, heat gently to expel the acids, dry, and ignite at the same temperature as for the initial residue. Fuse with a minimum of potassium bisulphate, cool, extract with water containing a few drops of sulphuric acid, and add to the main solution.

Residues containing much carbide, *e.g.*, carbon–chrome steels, etc., require a modified recovery treatment:

> Treat as detailed above, including the fusion with potassium bisulphate, but extract the fusion products with 50 ml. of sulphuric acid (1 : 9). Add ammonium hydroxide (1 : 1) until the hydroxides are just completely precipitated, boil, filter through a Whatman 541 12·5-cm. filter and wash with hot water. Remove the filter paper from the funnel, open it out over the beaker containing the main solution for electrolysis, and rinse the precipitate into the solution with a jet of water. If necessary, a small final rinse of the paper

with sulphuric acid (1 : 99) may be applied. Reserve the filtrate from the hydroxide precipitation and add it to the electrolyte after completion of the electrolysis.

(3) The current should be regulated to a maximum of 15 amp. until most of the iron is removed, and thereafter chromium removal is facilitated if no further regulation of the current is made, *i.e.*, it is permitted to rise in accordance with the changing p.d. across the electrodes.

(4) It is possible to detect the presence of 10 mg. of chromium by the colour of the solution.

APPENDIX II

Cleaning Mercury After Use as a Cathode in Electrolysis

Separation of Amalgam

Wash the mercury free from acid with water. Drain off as much water as possible and remove remaining traces by the use of filter-paper clippings. Using suction, filter the dry mercury through a clean Buchner-type glass funnel with sintered plate of porosity grade 1 into a dry pressure flask (Note 1) until a small pad of amalgam is formed on the filter. Return the filtered mercury to the original container and proceed with the filtration (Note 2). To remove 'tail,' strain the mercury through a hardened (No. 541) filter paper which has been punctured with a series of pin pricks, and store in clean dry containers until required for electrolysis.

Treatment of the Amalgam for the Recovery of Mercury

Transfer the amalgam from the filter to an iron pot still (Fig. 3) and separate the mercury by distillation. This operation must be carried out in a fume cupboard possessing ample ventilation. To remove 'tail,' strain the distillate through a hardened (No. 541) filter paper which has been punctured with a series of pin pricks, and transfer to clean dry containers until required for electrolysis.

Notes

(1) It is essential that all apparatus is clean (free from grease) and dry.

(2) When the depth of amalgam in the filter funnel is about 2 in. and filtration becomes sluggish, transfer the amalgam to an 800-ml. squat beaker by inverting the funnel and tapping gently. Reserve the amalgam for treatment. To clean the filter, pass *aqua regia* through it slowly. Wash well with water and dry at 105° C. before use.

HISTORICAL NOTE NO. 33

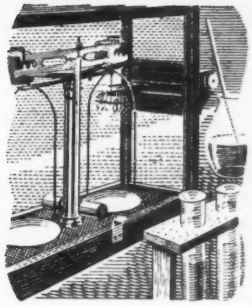
A Famous English Fireback of 1548

By H. R. Schubert

THE cast-iron fireback shown in the Figure represents the arms of King Edward VI (1547–1553) in a quartered shield (three fleurs-de-lys, three leopards) surmounted by a crown and with a griffin and a greyhound as supporters. The date at the base (1548) makes it the earliest dated fireback in England.

The fireback appears to have been much favoured in the sixteenth century. A specimen is at Ockwells, in Berkshire, and a fragment at Anne of Cleves' house at Lewes, in Sussex. The fireback was apparently in great favour on the Continent as well, since several specimens are preserved in Belgian and German museums, such as the Musée Archéologique at Namur, the Musée Curtius at Liége, and in the collection of firebacks of the Verein Deutscher Eisenhüttenleute at Düsseldorf, the last-named being acquired from Grand Hallieux, near Stavelot in Belgium. Another found at Libramont in Belgium, and now preserved at the Musée Archéologique at Arlon, only has one slight difference from those noted. The outlines lead from the sides directly into the top arch without any break.

Manuscript received 11th September, 1953. Dr. Schubert is Historical Investigator to The Iron and Steel Institute.



A Thermodynamic Study of the Iron, Cobalt, and Nickel Sulphides

By Terkel Rosenqvist

SYNOPSIS

The thermodynamics of the iron, cobalt, and nickel sulphides have been studied at temperatures between 400° and 1200° C. with hydrogen–hydrogen-sulphide equilibria and sulphur-pressure measurements. The stability ranges of the different sulphide phases and their free energies of formation have been determined.

In the iron–sulphur system the results indicate that FeS_2 has a peritectic decomposition point at about 800° C. and 25 atm. pressure.

In the cobalt–sulphur system the following phases were observed within the given temperature ranges: $Co_4S_3 \pm x$ (780–930° C.), Co_9S_8 (up to 835° C.), $CoS_1 + x$ (460° C.–m.p.), Co_3S_4 (up to 625° C.), and CoS_2.

In the nickel–sulphur system the following phases were observed: Ni_3S_2 (up to 555° C.), $Ni_3S_2 \pm x$ (525–810° C.), Ni_6S_5 (up to 560° C.), $NiS_1 + x$, and NiS_2.

The stability of the different sulphides decreases in the sequence iron sulphides to nickel sulphides. Simultaneously, the composition of the most stable sulphide shifts towards lower sulphur contents. The results are discussed, with emphasis on their connection with the structure of the different phases and the nature of the interatomic binding forces. 817

Introduction

THE equilibrium diagrams of the Fe–S, Co–S, and Ni–S systems have previously been studied by a number of investigators by means of thermal analysis, vapour-pressure measurements, and X-ray and metallographic methods. A survey of the results obtained before 1935 is given by Hansen.[1] More recent investigations will be referred to during the discussion of the individual systems.

The three sulphide systems are each characterized by a rather stable monosulphide which at high temperatures has the hexagonal NiAs structure. This phase is able to take an excess of sulphur into solid solution, and will therefore be symbolized in this paper by the formula AS_{1+x} (A = Fe, Co, or Ni). Hägg and Sucksdorff[2] have shown that the solid solubility is caused by a subtraction of metal atoms from the lattice.

In the monosulphides, particularly in FeS_{1+x}, various types of phase transformation and magnetic transformation appear at lower temperatures. These have been studied particularly by Haraldsen.[3] Although many questions are still open in this region, they are not covered by the present investigation.

All three systems show the presence of a disulphide phase, AS_2, with pyrite structure. Although there is some indication that iron disulphide deviates slightly from stoichiometric composition,[4] the range of solid solubility appears to be much smaller than that of the monosulphides.

Whereas iron forms only the mono- and disulphides, cobalt and nickel both form compounds of composition A_3S_4 with spinel structure,[5, 6] and they also form several compounds with less sulphur than the monosulphide.[1]

Complete liquid miscibility exists in all cases between the metal and the monosulphide. Nothing is known, however, about the extent of liquid miscibility at higher sulphur contents, because experimental difficulties are caused by the very high decomposition pressure at those compositions.

The thermodynamics of the iron, cobalt, and nickel sulphides have been studied by various investigators by several different methods. The data published before 1937 have been reviewed by Kelley.[7] Later data have been covered in a recent publication by Richardson and Jeffes.[8] Heats of formation determined by calorimetric methods, as well as specific-heat data for some of the sulphides, are listed by Kubaschewski and Evans.[9] These data are usually insufficient to make possible the accurate calculation of high-temperature free energies.

For such a purpose, vapour pressures and gas equilibrium data have proved to be of the greatest value. Biltz and his co-workers[4, 10, 11] studied the decomposition pressures of the disulphides FeS_2, CoS_2, and NiS_2 in equilibrium with the coexisting monosulphides. From their data, the free energies of formation of the disulphides from sulphur vapour and sulphur-saturated monosulphide can be calculated.

For the sulphides of lower sulphur content the vapour pressure is too low to be measured directly. Instead, the reaction with hydrogen to form hydrogen sulphide has been used, as, for example, $FeS + H_2 = Fe + H_2S$. When data for this equilibrium are

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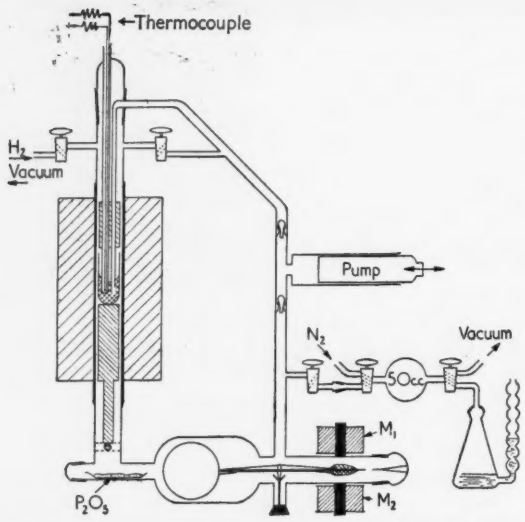

Fig. 1—Apparatus for gas–metal equilibrium studies

combined with well-known[7–9] equilibrium data for the dissociation of hydrogen sulphide, $2H_2S = 2H_2 + S_2$, the sulphur pressure and the free energy of formation of the lower metal sulphides from the elements may be calculated. Earlier investigations gave rather inconsistent results,[12, 13] but more recent data show good agreement with each other.[14, 15]

Unfortunately, most of the previous investigators did not state the exact compositions of their sulphide preparations. In the work on cobalt and nickel sulphides, particularly, it is uncertain which phases were actually present during the experiments.[13, 16]

In the present investigation, the vapour pressure and the gas ratio H_2S/H_2 are measured as functions of temperature and composition of the sulphide or sulphide mixture. The existence and extent of the different phases are determined from the way in which the escaping tendency of the sulphur varies with the composition of the sulphide. From the gas ratios and the sulphur pressures the free energies of formation of the different phases are obtained. This method therefore shows not only which phases are stable at a particular temperature and composition, but also how stable they are.

EXPERIMENTAL PROCEDURE

Materials

The different sulphides of iron, cobalt, and nickel were prepared from the elements. Cobalt and nickel metals were obtained by the reduction of their oxides with hydrogen at 700–900° C. The iron was carbonyl iron, treated with hydrogen at 700–900° C. to remove surface oxides.

Whereas the iron contained less than 0·1% of impurities, the cobalt contained about 0·5% of nickel and the nickel about 0·5% of cobalt. Since the two metals, as well as their sulphides, are chemically very similar and form solid solutions with each other, these impurities were not regarded as serious. In the preparation and analysis of the sulphides the sum of cobalt and nickel was considered to represent the content of the major constituent.

The various sulphides and intermediate alloys* were prepared by heating accurately weighed amounts of the metal and redistilled sulphur in evacuated and sealed Pyrex tubes at 500–600° C. For the lower sulphides, *i.e.*, for alloys with less than 50 at.-% of sulphur, this reaction was completed in a day or two. For the preparation of the higher sulphides the reaction was much slower and required several days and sometimes weeks.

The hydrogen, to be used for equilibrium measurements, was first purified in tank batches by passage through activated charcoal at liquid-nitrogen temperature under a pressure of 150 atm., so as to remove any hydrocarbons that might be present. Before use the hydrogen was further purified by passage through heated palladinized asbestos and was dried over phosphorus pentoxide.

Technique

The experimental method used for the lower sulphides has been described previously,[17] but certain modifications to the original apparatus have been made. The design finally arrived at is shown in Fig. 1.

The apparatus consisted of a closed, gas-tight system through which the gas could be circulated by means of a piston pump. The pump was made entirely of glass and had a tight-fitting piston lubricated with silicone oil. Provided that the gas pressure in the apparatus did not deviate strongly from that of the outside atmosphere, no gas leakage occurred in the pump.

The gas was pumped through a narrow mullite tube into the mullite furnace tube, in which was mounted an alumina crucible that contained a weighed amount of the metal sulphide (10–15 g.). For the solid sulphides the gas passed through the sulphide powder, and in the cases where the sulphide was molten the gas bubbled through the melt. A standardized Pt/Pt–Rh thermocouple, enclosed in a mullite tube, extended down into the crucible, and the temperature could be measured potentiometrically to within 1° C.

The temperature of the furnace was kept constant by means of either a Leeds and Northrup temperature controller, or a constant voltage transformer which maintained a constant heat input in the furnace. In most experiments the temperature was maintained constant to ± 2° C.

On leaving the furnace the gas passed over a boat containing phosphorus pentoxide, which removed traces of moisture formed by the slight reduction of the furnace refractories. The gas then passed through a chamber (lower right, Fig. 1) which contained a buoyancy balance, by means of which the density and subsequently the composition of the gas mixture were determined. The construction of the buoyancy balance and the method for computing the gas composition have been described previously.[17]

After the crucible with the sulphide alloy had been placed in the furnace, the apparatus was evacuated

* The term alloy will be used in this paper as a common term for all metal–sulphur preparations, regardless of whether they are homogeneous phases or two-phase mixtures.

with a mechanical pump, and the furnace was heated to about 100° C. Pure hydrogen was introduced and removed at least three times, to purge the apparatus thoroughly. With a slight over-pressure of hydrogen in the apparatus, and with the circulation pump working, the furnace was then heated to the desired temperature.

Equilibrium gas ratios were obtained by continuous circulation of the gas until the gas balance showed that no further change occurred in the gas density. This method has the advantage that the gas composition can be determined without the removal of any gas from the apparatus. Thus, a large number of consecutive measurements can be taken without consumption of hydrogen sulphide. This is particularly important for high gas ratios, where the removal of a gas sample, and subsequent admission of hydrogen to the apparatus and re-establishment of equilibrium, would cause a marked change in the composition of the sulphide.

The buoyancy balance had an accuracy corresponding to about 0·1% of H_2S and was therefore inadequate for the measurement of H_2S/H_2 ratios below 10^{-2}. In this range, therefore, gas samples were taken for chemical analysis. A gas sample was sucked into an evacuated glass bulb of known volume (about 50 c.c.), and was subsequently flushed into an absorption vessel by means of an inert gas (nitrogen or argon). The gas sample was absorbed in alkaline potassium hypochlorite solution, and the amount of hydrogen sulphide was determined by iodometric titration according to the method recently described by Dunicz and Rosenqvist.[18] From the data for the volume, temperature, and pressure of the gas sample the H_2S/H_2 ratio could then be calculated, and from a number of consecutive analyses the attainment of equilibrium could be ascertained.

For gas ratios of the order of 10^{-4}, the gas in the whole apparatus, about 1·5 litres, was flushed into the absorption flask by means of helium and was then analysed. In these cases the attainment of equilibrium could not be checked by consecutive analysis but was ascertained by approaching the equilibrium conditions from the side of high as well as low gas compositions.

The greatest obstacle in earlier investigations of this kind has been thermal diffusion in the gas mixture; *i.e.*, the Soret effect has caused the heavier gas, hydrogen sulphide, to be preferentially enriched in the cold part of the apparatus, and the gas ratio analysed in the cold zone has therefore been higher than that in the hot zone. By increasing the rate of circulation, and by the use of narrow tubes to and from the hot zone, this effect can be virtually eliminated. In the present case a 4-mm. dia. inlet tube was used, and the outlet was constricted by means of a ceramic plug which left only a narrow gas passage. To determine the influence of the gas velocity on the thermal diffusion, some runs were made with different pumping rates. It was found that the gas ratio remained constant for pumping rates from 175 c.c./min. (the lowest rate at which the pump could operate) up to 440 c.c./min. When the circulation was arrested, however, the gas ratios in the cold zone increased by 50–100%, depending on the temperature of the hot zone. For this investigation, therefore, pumping rates between 300 and 400 c.c./min. were used.

In addition to hydrogen and hydrogen sulphide, the gas in the hot zone will contain a small amount of sulphur vapour, in equilibrium with the gas mixture. On cooling, this will react with hydrogen and the H_2S/H_2 ratio will be slightly increased. A method of correcting for this increase and of calculating the gas ratio in the hot zone has been described previously.[17] For some sulphides with rather high sulphur pressures the sulphur did not react completely with hydrogen on cooling, but a small amount condensed on the tube wall in the cold zone. Although this sulphur loss was very small and did not affect the gas ratio, it was necessary to determine the composition of the sulphide sample by analysis after the end of each experiment.

The experimental runs were carried out at temperatures between 400° and 1300° C. Except for the runs at 400–500° C., the time required to reach a constant gas composition was independent of the furnace temperature and amounted to a few hours. This shows that the limiting factor was not the reaction rate but the time needed to mix the gas thoroughly.

After the equilibrium gas ratio had been determined at one temperature, the temperature could be changed, and the gas ratio could be obtained as a function of temperature for a sulphide of practically constant composition. In many cases, however, the temperature was maintained constant, the system was evacuated, and fresh hydrogen was introduced. When equilibrium was again established the sulphur content of the sulphide had decreased somewhat, owing to the transfer of sulphur to the atmosphere. When this operation was repeated, the gas ratio was obtained as a function of sulphide composition for a constant temperature.

After one experimental ' run ' had been completed the sulphide was analysed for its metal and sulphur contents. The sum of the two was usually 99·5–100%. The missing fraction of a percent. was added proportionally to the metal and the sulphur, to make their sum total exactly 100%. The composition of the sulphide at any time could be calculated from the composition of the original alloy, the composition determined after the experiment, the gas composition at any time, and the amount of gas that had been removed during the experiment. The sulphur content could drop by several per cent. during the experiment. As the sulphur loss unaccounted for in the material balance was less than 0·2%, the calculated compositions are considered to be correct to within 0·2% S.

This gas-circulation apparatus was used for sulphides that had gas ratios up to about 0·5. In exceptional cases, *i.e.*, at reduced pressures, it could be used for gas ratios up to unity. For sulphides with higher sulphur pressures other techniques were used.

For the higher cobalt and nickel sulphides, in the temperature range 400–650° C., the H_2S/H_2 ratio was determined by means of a simple gas-analysis apparatus in which the main emphasis was put on the measurement of the minor constituent, hydrogen. The hydrogen sulphide was then obtained by difference.

The apparatus consisted of a bulb of silica-rich glass (Vycor), with a volume of about 200 c.c., which

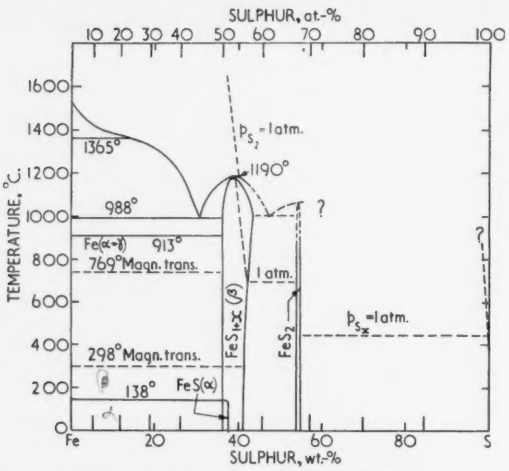

Fig. 2—The system iron–sulphur

was completely enclosed in an electric furnace, the temperature gradient inside the bulb being less than 5° C. The outlet tube was almost completely filled by the thermocouple tube, which left only a narrow gas passage.

The bulb was connected to a gas burette by means of capillary tubes. The burette contained 50% phosphoric acid solution as manometric fluid. (Phosphoric acid was found to be well suited for this purpose, as it has a low vapour pressure and is chemically inert towards hydrogen sulphide.) About 10 g. of the sulphide was placed in the bulb. The latter was then evacuated and purified hydrogen was admitted. By repeated evacuation and hydrogen admission the bulb was thoroughly purged.

When the bulb was heated the sulphide reacted with the gas to give the equilibrium gas mixture. As there was no significant temperature gradient inside the bulb, thermal diffusion was eliminated.

Before a gas sample was taken the gas inside the capillary leads was disposed of, after which a gas sample of about half the entire gas volume was sucked into the gas burette. The gas was then transferred to an absorption pipette, where the hydrogen sulphide was absorbed in a 25% potassium hydroxide solution. The residual hydrogen was then measured. This procedure was particularly well suited for H_2S/H_2 ratios from about unity to about 20, *i.e.*, down to about 5% hydrogen in the gas. For higher gas ratios the accuracy was poorer, owing to the difficulty in measuring the small hydrogen volumes.

After each analysis more hydrogen was admitted to the bulb to make up for the gas removed, and the experiment was continued.

To determine the time needed to establish equilibrium, gas samples were taken after various periods, and it was found that the values obtained after 4 hr. were the same as those after 12 hr. A period of 12 hr. was therefore considered to be adequate for equilibrium to be established, and all subsequent experiments were of this duration.

After the completion of a series of measurements the residual sulphide was analysed. Since the initial composition of the sulphide was known, as well as the amount of sulphur removed for each analysis, the composition corresponding to each gas analysis could be calculated.

For the higher iron sulphides, up to FeS_2, the sulphur pressure was measured by means of a simple dew-point method. The apparatus consisted of a silica tube ($\frac{1}{2}$ in. by 7 in.) with thermocouple wells in both ends. After about 10 g. of the sulphide alloy had been placed in the tube the latter was evacuated, sealed, and placed in a furnace, with separate heating coils for the two ends. While the temperature of the sulphide was kept constant, the temperature of the other end was adjusted to that at which sulphur condensed and evaporated within about 2° C. As the vapour pressure of pure liquid sulphur is known from the work of West and Menzies,[19] the decomposition pressure of the sulphide could be derived. This method is similar in principle to the method used by

Table I

REDUCTION OF IRON SULPHIDES WITH HYDROGEN

Experiment No.	Sulphur, wt.-%	Temp., °C.	$\frac{H_2S}{H_2} \times 10^2$	Phases Present*
Fe(S)–24	21·0	500	0·015	Fe + FeS
		700	0·073	
		900	0·333	
		800	0·183	
		700	0·089	
		600	0·043	
		800	0·189	
		988	0·524	Fe + FeS + (liq)
		1100	0·675	Fe + liq
		1200	0·798	
		1250	0·835	
		795	0·170	Fe + FeS
		695	0·092	Fe + FeS
Fe(S)–25	20·0	900	0·318	Fe + FeS
		1000	0·541	Fe + liq
		1170	0·773	Fe + liq
		1340	0·987	liq
		1094	0·713	Fe + liq
		984	0·529	Fe + FeS
Fe(S)–26	37·2	800	6·02	FeS_{1+x}
	37·2	970	6·70	
	37·2	992	6·53	
	36·9	990	2·42	FeS + liq
	36·6	1102	3·85	
	36·7	1100	3·57	
	36·5	1114	4·60	
	36·6	1105	3·80	
	36·6	1103	3·87	
	36·1	1103	3·70	
	36·5	988	0·58	(Fe) + FeS + liq
Fe(S)–27	37·5	700	8·62	FeS_{1+x}
	37·4	804	10·15	
	37·3	1100	11·48	
	36·9	1100	6·67	FeS + liq
	36·6	1104	4·20	
	36·4	1105	4·40	
	36·0	1154	11·32	
	36·0	1150	10·99	
	36·5	1050	2·55	
	36·5	990	1·0	FeS

* Doubtful phases are given in parentheses

Allen and Lombard[20] for the determination of the dissociation pressure of CuS and FeS_2. It is considerably simpler than the manometric method used by Juza and Biltz,[4] and because of its ruggedness it can be used to measure pressures of several atmospheres.

Owing to the amount of sulphur given off to the atmosphere, the sulphur content of the sulphide will be slightly altered during the experiment. This correction was calculated from the sulphur pressure and the temperature distribution in the tube, in connection with the vapour-density data given by Preuner and Schupp.[21] The correction amounted to a maximum of 0·2% in the composition of the alloy.

The vapour density of the gas increased markedly from the hot region, where it corresponded mainly to S_2 molecules, to the colder region, where it corresponded mainly to S_8 molecules. It was assumed, however, that by steady-state conditions equality existed between the total sulphur pressures in the two ends, and not between the partial pressures of the different molecular species.

THE SYSTEM IRON–SULPHUR

The equilibrium diagram shown in Fig. 2 is based on the data surveyed by Hansen[1] and the work on thermal analysis by Jensen.[22]

The gas equilibrium $FeS + H_2 = Fe + H_2S$ has previously been studied by several investigators. Rather large discrepancies exist between the earlier work by Britzke and Kapustinskii[12] and Jellinek and Zakowski[13] and the recent work by Sano,[23] Sudo,[15] and Alcock and Richardson.[14] Intermediate values were found by Cox and his co-workers.[24] As pointed out by Alcock and Richardson, some of the earlier work suffered distinctly from thermal-diffusion errors.

This equilibrium was studied in the present work on alloys with about 20% of sulphur, *i.e.*, about equal amounts of the two solid phases. The results of these measurements are given in Table I.

For temperatures above the eutectic temperature of 988° C., experiments Fe(S)–24 and 25 (Table I) give the gas ratio for equilibrium between solid iron and the sulphide melt. Experiments Fe(S)–26 and 27 give some data for the equilibrium between solid FeS_{1+x} and the melt.

These experiments also give data for the homogeneous solid sulphide phase. They are best seen in Fig. 3, in which the gas ratio is plotted logarithmically as a function of the sulphur content at some constant temperatures. These curves were drawn partly through experimental points obtained at that particular temperature and partly through values obtained by interpolation between experimental points for closely adjacent temperatures.

From the intersection of the curves for the homogeneous phase and the curves for the two-phase equilibrium, the lower limit of the homogeneous phases is found to correspond to about 36·4% (49·9 at.-%) of sulphur, *i.e.*, very closely to the stoichiometric composition FeS.*

At the very early stage of the present investigation, before the experimental difficulties had been completely overcome, several measurements were carried out at 1000–1200° C. on sulphide melts containing 20–36% of sulphur. It was later shown that these data were 10–25% too high, owing to thermal diffusion errors. Some of these values, corrected for this error, are shown in Fig. 3 as broken curves. They show the same general trend as was found by Maurer, Hammer, and Möbius[25] for Fe–S melts in the same temperature and composition range. Below 30% S the gas ratio increases very slowly with increasing sulphur content of the melt. At higher sulphur contents the increase is more rapid, and as the stoichiometric composition (36·5% S) is approached the gas ratio increases by a factor of three (at 1200° C.) for every unit wt.-% increase in the sulphur content of the melt.

Figure 3 also includes the gas ratios for the solutions of sulphur in solid iron as determined by Rosenqvist and Dunicz.[26] Their values for the gas ratios at solid saturation agree well with those obtained for two-phase alloys containing 20–36% of sulphur.

For sulphides of higher sulphur content, up to FeS_2, the sulphur pressure is too high to be measured by the gas equilibrium method. Instead, some

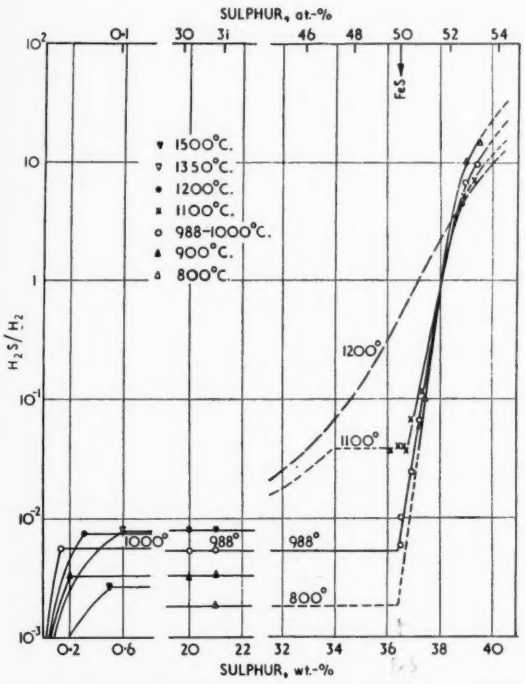

Fig. 3—Relationship between gas ratio and sulphur content for the system iron–sulphur at constant temperatures

* In a preliminary communication on this subject, presented at the Seventh Inter-Scandinavian Chemistry Conference in Helsinki in 1950, the author gave the lower limit of the FeS phase as about 35·5% S at 800–1000° C. Subsequent work has shown that this value was incorrect because of unsatisfactory experimental and analytical techniques. The data presented in the present paper, for this concentration range, are rather few, and further experimental work is required.

Table II

SULPHUR PRESSURES OF PYRITE AND PYRRHOTITE

Sulphur, wt.-%	Temp., °C.	Dew Point, °C.	p_{S_2}, atm.	H_2S/H_2	Phases Present
39·00	706	212	0·0043	13·0	FeS_{1+x}
38·99	800	264	0·022	10·4	
39·00	797	256	0·017	9·3	
38·98	905	312	0·079	7·9	
38·96	990	359	0·224	7·1	
38·99	898	304	0·066	7·7	
38·96	1021	366	0·253	6·1	
38·95	1025	371	0·278	6·2	
38·92	1079	398	0·461	5·7	
38·99	800	260	0·020	9·9	
38·97	982	349	0·179	6·7	
38·84	1190	451	1·09	4·7	FeS_{1+x} + liq
39·49	800	290	0·046	15·0	FeS_{1+x}
39·49	820	292	0·049	12·6	
39·47	900	341	0·147	11·1	
39·48	888	332	0·124	11·3	
39·42	990	394	0·435	9·9	
39·40	1051	436	0·868	9·3	
39·30	1100	457	1·19	8·1	
46·0	635·5	287	0·042	87	FeS_{1+x} + FeS_2
	634·5	285·5	0·040	86	
	633·5	284·5	0·039	86	
	667	347·5	0·171	119	
	676	377·5	0·329	146	
	675	373·5	0·296	142	
	684	422·5	0·710	196	
	596	228	0·0074	64	
	632·5	283	0·037	86	
	633	284	0·038	86	
	654	325	0·107	108	
	675·5	355	0·191	114	
	698·5	450	1·09	215	
	702	486	1·59	240	
	714	508	2·39	252	
	729·5	524	2·96	241	
	757·5	588	6·32	264	
50·0	644	270	0·026	62	FeS_{1+x} + FeS_2
	662·5	394·5	0·178	124	
	670·5	359·5	0·224	128	
	654·5	315·5	0·087	97	
	680·5	366·5	0·256	122	
	690·5	416·5	0·645	171	

measurements were made by means of the dew-point apparatus described on p. 40. The results are given in Table II for the solid solutions FeS_{1+x} as well as for two alloys that contain about equal amounts of FeS_{1+x} (pyrrhotite) and FeS_2 (pyrite). By interpolation between the data obtained for different compositions and temperatures, the sulphur pressure for constant compositions could be obtained as a function of temperature, as well as for constant temperatures as a function of composition. A rough extrapolation of the values obtained for the pyrrhotite phase shows that the upper limit of this phase corresponds to about 43 wt.-% S at 700–800° C.

For the two-phase alloys $FeS_{1+x} - FeS_2$, the sulphur pressure may be approximately fitted by the expression:

$$\log p_{S_2} = -\frac{19{,}000}{T} + 19{\cdot}60.$$

This corresponds to a decomposition temperature for pyrite ($p_{S_2} = 1$ atm.) of 697° C. For the dissociation of FeS_2 the vapour pressures are somewhat lower than those obtained by Allen and Lombard,[20] Raeder,[27] and de Rudder,[28] whereas they are about half the values measured by Juza and Biltz.[4] Also, for the homogeneous FeS_{1+x} phase the values are slightly lower than those measured by Juza and Biltz.

Although the work by Juza and Biltz was very carefully done, their values may be high, owing to the presence of gaseous impurities (*e.g.*, SO_2 evolved by reaction with traces of oxides). Such impurities would affect the manometric readings considerably more than they would affect the determinations by the dew-point method.

In the present investigation no attempt has been made to measure the width of the pyrite phase region. The data by Juza and Biltz suggest that a range of solid solution exists; as the vapour pressure is very slowly established in this composition range, however, their data may suffer from hysteresis effects.

To express the sulphur pressure of the high-sulphur alloys in the same units as for the low-sulphur alloys, the corresponding H_2S/H_2 ratios were calculated from the known data for the equilibrium $2H_2 + S_2 = 2H_2S$. This was done primarily because the H_2S/H_2 ratios are much less temperature-dependent than the sulphur pressures, and it made it possible to plot the effect of temperature without too much distortion or loss in precision. Furthermore, since the gas ratio represents the pressure of one atom of sulphur, it should show a simpler relationship than does the diatomic sulphur pressure to the sulphur content of sulphide phases where the sulphur occurs as isolated particles.

In Fig. 4, which summarizes the work for the entire iron–sulphur system, the gas ratio is plotted on a logarithmic scale against the inverse of the absolute temperature. The heavy curves correspond to the different two-phase equilibria, and the slope of these curves corresponds to the heat of the corresponding reaction; *e.g.*, $Fe + H_2S = FeS + H_2$. The fine curves correspond to constant compositions within a homogeneous phase, and the slope of these curves corresponds to the heat of solution of sulphur referred to hydrogen sulphide as reference; *e.g.*, $H_2S = S$ (in FeS) $+ H_2$.

The curves for the solid solutions are taken from the work of Rosenqvist and Dunicz,[26] and those for the solutions of sulphur in liquid iron from the work of Sherman, Elvander, and Chipman.[29]

Although the two-phase equilibrium pyrite–liquid-sulphur was not investigated, qualitative tests indicated that liquid sulphur is able to dissolve a small quantity of iron at 500° C.* In this case the sulphur pressure of the two-phase equilibrium would be somewhat less than for pure liquid sulphur. For lack of exact data, however, the sulphur pressure of pure liquid sulphur was taken. This is given by West[30]

* In an evacuated and sealed Pyrex tube a rod of iron was heated to 500° C. with a large excess of sulphur. On tilting the tube the liquid was drained off the sulphurized iron rod. This liquid, which appeared to be homogeneous at 500° C., solidified with a number of black spots. This sulphur was taken out of the tube, and after ignition it left a red residue of iron oxide.

for temperatures up to the critical point of liquid sulphur (about 1040° C.). His paper also gives the partial pressure of S_2 in saturated vapour, from which the corresponding H_2S/H_2 ratio was calculated.

The most interesting observation derived from Fig. 4 is that the curves for the decomposition of FeS_2 and for liquid sulphur converge strongly, and a slight extrapolation indicates that they will intersect at about 800° C., corresponding to an H_2S/H_2 ratio of 340 and a sulphur pressure of about 25 atm. This means that at this temperature pyrite would undergo a peritectic decomposition to give pyrrhotite and liquid sulphur. This conclusion is in direct conflict with the statement by Jensen[22] that pyrite has a congruent melting point above 1000° C. To clarify this point, further work with high-pressure equipment is needed.

On the whole, it is difficult to say much about the equilibrium relations in this part of the diagram. An interesting question is whether a region of liquid immiscibility exists between iron sulphide and sulphur, or whether the two melts are completely miscible. For simplicity the latter possibility is indicated in Fig. 4.

Thermodynamic Calculations

Between 500° and 988° C. (eutectic temperature) the gas ratio for the reaction $Fe + H_2S = FeS + H_2$ may be fitted by the expression

$$\log(H_2S/H_2) = -\frac{3100}{T} + 0{\cdot}179.$$

The corresponding Gibbs free energy is then

$$\Delta G^\circ = -14{,}170 + 0{\cdot}82\,T \text{ cal.}$$

When this is combined with the free energy for the reaction $2H_2 + S_2 = 2H_2S$, *viz.*,

$$\Delta G^\circ = -43{,}160 + 23{\cdot}61\,T \text{ cal.}$$

(a linear expression according to Richardson and Jeffes[8]), the free energy for the reaction $2Fe + S_2 = 2FeS$ is seen to be

$$\Delta G^\circ = -71{,}500 + 25{\cdot}25\,T \text{ cal.} \quad \ldots\ldots\ldots\ldots(1)$$

This is in very good agreement with the data by Sudo[15]:

$$\Delta G^\circ = -71{,}250 + 24{\cdot}62\,T \text{ cal.}$$

and by Alcock and Richardson[14]:

$$\Delta G^\circ = -71{,}820 + 25{\cdot}12\,T \text{ cal.}$$

Equation (1) represents an average for the range 500–988° C. For a more accurate expression that may be extended to room temperatures, the specific heats as well as the latent heats of the phase, and the magnetic transformations of iron and iron sulphide, must be taken into consideration. These data are listed by Kubaschewski and Evans[9]:

Fe(α)	$C_p = 3{\cdot}90 + 6{\cdot}80 \times 10^{-3}T$	(273–1033° K.)
α → β	Magnetic trans. $\Delta H^\circ = 660$ cal.	(1033° K.)
Fe(β)	$C_p = 9{\cdot}85$	(1033–1183° K.)
β → γ	Phase trans. $\Delta H^\circ = 220$ cal.	(1179° K.)
Fe(γ)	$C_p = 7{\cdot}55 + 1{\cdot}14 \times 10^{-3}T$	(1183–1674° K.)
FeS(α)	$C_p = 2{\cdot}03 + 39{\cdot}0 \times 10^{-3}T$	(273–411° K.)
α → β	Phase trans. $\Delta H^\circ = 1050$ cal.	(411° K.)
FeS(β)	$C_p = 12{\cdot}05 + 2{\cdot}73 \times 10^{-3}T$	(411–1473° K.)
S_2	$C_p = 7{\cdot}75 + 0{\cdot}888 \times 10^{-3}T$	(300–1500° K.)

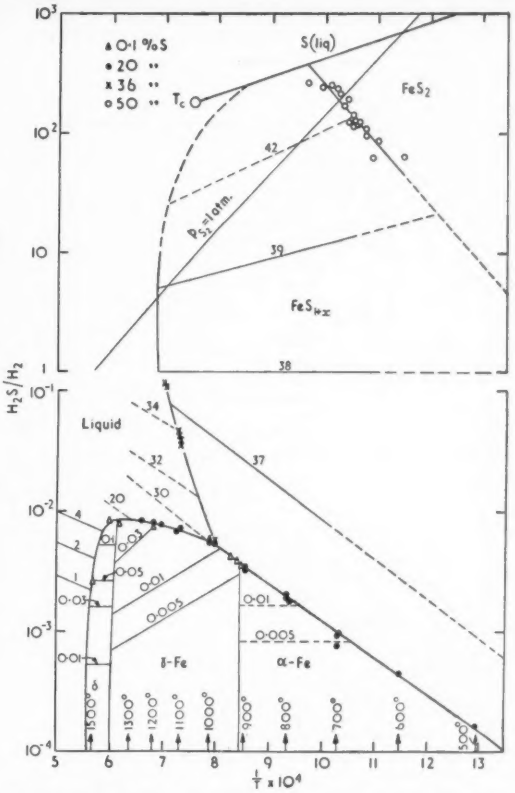

Fig. 4—Plot of H_2S/H_2 *versus* $1/T$ for the system iron–sulphur. (Compositions of alloys are in wt.-% of sulphur)

It appears that, at temperatures above the transformation point of iron sulphide, the variation in the heat of reaction due to the difference in specific heats of the components is almost exactly offset by the heats of transformation of iron. Thus, for the reaction $2Fe(\alpha \rightarrow \gamma) + S_2 = 2FeS(\beta)$,

$$\int_{411^\circ\text{K.}}^{1261^\circ\text{K.}} \Delta C_p dT = 1780 \text{ cal.},$$

and for 2Fe,

$$\Sigma \Delta H_{\text{trans.}} = 1760 \text{ cal.}$$

As the difference is well within the limits of the experimental data, one linear expression for the free energy may be used for the entire temperature range from the transformation point of iron sulphide (138° C.) to its melting point (1190° C.):

$$2Fe(\alpha \rightarrow \gamma) + S_2 = 2FeS(\beta)$$
$$\Delta G^\circ = -71{,}500 + 25{\cdot}25\,T \text{ cal.} \quad \ldots\ldots\ldots\ldots(1)$$

From this expression the following values for the heat and free energy of reaction at 411° K. (138° C.) are obtained:

$$\Delta H^\circ_{411^\circ\text{K.}} = -71{,}500 \text{ cal.}$$
$$\Delta G^\circ_{411^\circ\text{K.}} = -61{,}120 \text{ cal.}$$

For the formation of 2FeS(α) at the same temperature, therefore,

$$\Delta H^\circ_{411^\circ\text{K.}} = -73{,}600 \text{ cal.}$$
$$\Delta G^\circ_{411^\circ\text{K.}} = -61{,}120 \text{ cal.}$$

Table III
REDUCTION OF COBALT SULPHIDES WITH HYDROGEN

Experiment No.	Sulphur, wt.-%	Temp., °C.	$\frac{H_2S}{H_2} \times 10^2$	Phases Present*
Co(S)–4	30·3	750	0·8	$\alpha + \gamma$
	30·3	755	0·89	$\alpha + \gamma$
	29·9	850	4·5	β
	29·8	915	6·0	liq + β
	29·9	840	4·0	β
	29·8	910	5·6	β
	29·4	1040	10·1	liq
	29·3	1150	12·3	liq
	29·1	1250	13·7	liq
	29·5	985	8·7	liq
	29·6	955	7·9	liq
Co(S)–5	19·9	750	1·0	$\alpha + \gamma$
	19·9	850	1·6	$\alpha + \beta$
	19·9	960	1·9	α + liq
	19·8	1110	2·2	α + liq
	19·8	1250	2·6	α + liq
Co(S)–6a	33·0	615	19·5	γ + (δ)
	33·5	690	13·1	$\gamma + \delta$
	33·8	750	8·7	$\gamma + \delta$
	33·9	760	8·4	$\gamma + \delta$
	34·0	845	6·2	$\beta + \delta$
	34·0	865	7·5	$\beta + \delta$
	34·0	852	6·8	$\beta + \delta$
	33·5	925	12·9	$\beta + \delta$
	33·3	950	15·9	liq + δ
	32·8	970	23·0	liq + δ
	32·8	965	22·7	liq + δ
6b	31·3	967	18·1	liq
	31·7	915	12·2	$\beta + \delta$
	32·2	840	5·9	$\beta + \delta$
	32·2	850	6·5	$\beta + \delta$
Co(S)–7a	33·5	650	26·6	$\gamma + \delta$
	34·3	702	15·9	$\gamma + \delta$
	34·9	777	8·0	$\gamma + \delta$
	34·2	834	5·2	$\beta + \gamma + \delta$
	34·9	882	8·4	$\beta + \delta$
	34·9	879	7·9	$\beta + \delta$
	34·4	937	13·8	liq + $\beta + \delta$
	33·7	973	23·9	liq + δ
	32·7	1009	41·4	liq + δ
7b	31·5	932	12·5	$\beta + \delta$
	31·9	880	7·4	$\beta + \delta$
	32·2	836	5·1	β + (γ) + δ
	32·2	830	4·4	$\beta + \gamma$
Co(S)–8a	31·8	788	1·5	$\beta + \gamma$
	31·7	806	2·2	$\beta + \gamma$
	31·6	820	3·7	$\beta + \gamma$
	31·5	835	5·1	$\beta + \gamma + \delta$
	31·1	902	9·9	$\beta + \delta$
8b	30·4	903	7·5	β
	30·3	919	8·0	β
	30·1	934	10·4	liq
	30·0	1005	12·3	liq
	29·7	1036	14·9	liq
	30·6	835	5·0	β
Co(S)–9	27·6	703	0·6	$\alpha + \gamma$
	27·6	775	1·1	$\alpha + \gamma$
	27·5	873	1·8	α + (liq) + β
	27·5	883	2·1	liq + β
	27·4	890	2·3	liq + β
	27·4	900	2·7	liq
	27·4	918	2·9	liq
	27·3	1000	4·0	liq
	27·2	1100	5·1	liq
	27·1	1200	6·0	liq
	27·0	1257	6·8	liq
	27·5	835	1·6	$\alpha + \beta$
Co(S)–10a	33·7	640	28·6	$\gamma + \delta$
	34·2	678	20·4	$\gamma + \delta$
	34·9	642	11·0	$\gamma + \delta$
	35·2	797	6·6	$\gamma + \delta$
	35·3	825	5·4	$\gamma + \delta$
	35·3	834	5·3	(β) + $\gamma + \delta$
	34·7	935	14·0	liq + $\beta + \delta$
	33·1	1002	38·7	liq + δ
10b	32·0	935	12·9	liq + $\beta + \delta$
	31·0	1000	25·5	liq
	30·8	1100	28·4	liq
Co(S)–11	16·3	600	0·17	$\alpha + \gamma$
	16·3	700	0·43	$\alpha + \gamma$
	16·1	783	1·07	$\alpha + \gamma$
	16·1	873	1·49	α + liq
	16·0	1005	1·85	α + liq
	16·0	1138	2·2	α + liq
	16·0	1260	2·1	α + liq
Co(S)–12a	34·6	663	24·4	$\gamma + \delta$
	35·3	722	13·7	$\gamma + \delta$
	35·7	800	9·5	δ
12b	35·2	812	5·6	$\gamma + \delta$
	35·2	848	5·4	$\beta + \delta$
	34·2	697	17·4	$\gamma + \delta$
12c	32·8	605	13·4	γ
	32·8	700	13·1	γ
	33·3	775	7·3	$\gamma + \delta$
	33·5	835	4·9	$\beta + \gamma + \delta$
	32·8	650	13·4	γ
Co(S)–13a	32·7	677	17·4	γ
	33·1	725	12·2	$\gamma + \delta$
	33·9	800	6·2	$\gamma + \delta$
	33·7	836	4·9	$\beta + \gamma + \delta$
13b	33·2	818	5·4	$\gamma + \delta$
	33·0	760	8·3	γ
	32·8	700	9·9	γ
	32·8	600	10·7	γ
13c	32·7	700	0·5	(α) + γ
Co(S)–14	26·0	600	0·19	$\alpha + \gamma$
	25·9	788	1·13	$\alpha + \beta$
	25·8	858	1·55	$\alpha + \beta$
	25·8	950	2·0	α + liq
	25·8	1010	2·2	α + liq
	25·7	1130	2·8	liq
	25·6	1267	4·1	liq
Co(S)–15a	36·2	700	90·4	δ
15b	36·1	700	29·5	δ
	36·1	800	31·0	δ
	35·9	900	34·4	δ
	35·6	1004	40·5	liq + δ
15c	35·7	910	23·4	δ
	35·9	800	20·5	δ
	36·1	700	17·0	$\gamma + \delta$

* The phases are: α = Co, $\beta = Co_4S_{3\pm x}$, $\gamma = Co_9S_8$, $\delta = CoS_{1+x}$. Doubtful phases are given in parentheses

If the values for the specific heats below 138° C. are introduced, the free energy will be given by the expression

$$\Delta G^\circ_{273\text{–}411^\circ\,K.} = -74{,}240 + 26{\cdot}44T\log T - 31{\cdot}76 \times 10^{-3}T^2 - 24{\cdot}12T.$$

This gives for the reaction $2Fe(\alpha) + S_2 = 2FeS(\alpha)$ at 25° C. (298° K.):

$$\Delta H^\circ_{298^\circ\,K.} = -74{,}850 \text{ cal.}$$
$$\Delta G^\circ_{298^\circ\,K.} = -64{,}740 \text{ cal.}$$

For the reaction $S_2 = 2S(rh)$ the following heat and free energy apply[8]:

$$\Delta H^\circ_{298^\circ\,K.} = -31{,}020 \text{ cal.}$$
$$\Delta G^\circ_{298^\circ\,K.} = -19{,}360 \text{ cal.}$$

For the reaction $Fe(\alpha) + S(rh) = FeS(\alpha)$, therefore,

$$\Delta H^\circ_{298^\circ\,K.} = -21{,}900 \text{ cal.}$$
$$\Delta G^\circ_{298^\circ\,K.} = -22{,}700 \text{ cal.}$$

These values may be compared with those listed by Kubaschewski and Evans[9]:

$$\Delta H^\circ_{298^\circ\,K.} = -22{,}900 \text{ cal.}$$
$$\Delta G^\circ_{298^\circ\,K.} = -24{,}500 \text{ cal.}$$

and by the National Bureau of Standards[31]:

$$\Delta H^\circ_{298^\circ\,K.} = -22{,}720 \text{ cal.}$$
$$\Delta G^\circ_{298^\circ\,K.} = -23{,}320 \text{ cal.}$$

Within the homogeneous pyrrhotite phase, the partial free energy of sulphur, referred to a mixture of equal amounts of hydrogen and hydrogen sulphide, is given by the equation

$$\Delta\mu_S = RT\ln(H_2S/H_2).$$

The partial free energies for the following compositions are given by:

37 wt.-% S,	$\Delta\mu_S$ =	−15,000	+ 5·5 × T	cal.
38 wt.-% S,	$\Delta\mu_S$ =	0	+ 0 × T	cal.
39 wt.-% S,	$\Delta\mu_S$ =	+ 5000	+ 0 × T	cal.

In these expressions, the first term on the right-hand side gives the heat of solution, $\Delta\bar{H}_S$, and the second term gives the negative entropy of solution, $-\Delta\bar{S}_S$. Owing to the rapid increase in gas ratio with changing composition of the pyrrhotite phase, the heat term may be uncertain to within 1–2 k.cal. and the entropy term to within 1–2 entropy units. It appears that, whereas the heat of solution increases by about 20 k.cal. between 37 and 39 wt.-% S, the entropy of solution remains practically constant. This corresponds to the idea that the structural distribution of the sulphur atoms remains constant whereas the binding energy decreases considerably.

From the sulphur vapour pressure of pyrite the free energy of the reaction $2FeS_{1+x} + S_2 = 2FeS_2$ is calculated:

$$\Delta G^\circ = -87{,}000 + 89{\cdot}7T \text{ cal.}*$$

THE SYSTEM COBALT–SULPHUR

This system contains a number of different sulphide phases. In the low-sulphur range, thermal analyses[1, 32] have shown the existence of: $Co_4S_{3\pm x}$ stable between about 787° and 932° C.; Co_9S_8 stable up to 832° C.; and the monosulphide CoS_{1+x} stable up to its melting point—about 1150° C.

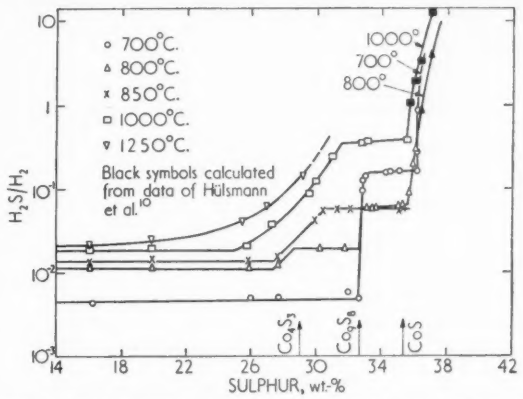

Fig. 5—Relationship between gas ratio and sulphur content for the system cobalt–sulphur at constant temperatures

X-ray investigations by Lundqvist and Westgren[5] showed that the second phase corresponded more closely to the formula Co_9S_8. These investigators also found that the monosulphide was stable between 51 and 53 at.-% S, and that in the high-sulphur range the phases Co_3S_4 and CoS_2 existed. Hülsmann, Biltz, and Meisel,[10] who measured the decomposition pressure of CoS_2 at 700–760° C., were unable to confirm the existence of Co_3S_4. This conflict was later solved by Heimbrecht, Biltz, and Meisel,[33] who showed that Co_3S_4 is stable only below 680° C., *i.e.*, below the temperature at which the decomposition pressure had been measured.

Schenck and von der Forst[34] measured the H_2S/H_2 equilibrium in the limited range Co_9S_8–Co_3S_4 at a single temperature, 400° C. For the lower sulphides some gas equilibrium measurements have also been made by Jellinek and Zakowski[13] and by Sudo.[16] These authors did not state the compositions of their sulphide alloys, but assumed that their measurements corresponded to equilibrium between CoS and Co—an equilibrium which is impossible, owing to the presence of lower sulphides.

In the present investigation, alloys with up to 37 wt.-% (52 at.-%) of sulphur were studied with the gas circulation apparatus. The results of these experiments are given in Table III.

Figure 5 gives the gas ratio as a function of composition for a number of selected temperatures. For the homogeneous phase CoS_{1+x} these curves were supplemented with the vapour-pressure data determined by Hülsmann and co-workers,[10] recalculated to give the corresponding H_2S/H_2 ratios.

Phase Relations

Figure 5 shows clearly the presence of the different sulphide phases, which are characterized by sudden changes in the gas ratios. The phase $Co_4S_{3\pm x}$, which is unstable at 700° C., appears clearly at 800° and 850° C. At the latter temperature it is stable between 27·5 and 30·5 wt.-% (41·1–44·7 at.-%) of sulphur.

* This equation is strictly stoichiometric with respect to sulphur only. If the saturated pyrrhotite phase contains 43 wt.-% S, the equation will read :

$$2{\cdot}86FeS_{1{\cdot}3} + S_2 = 2{\cdot}86\ FeS_2.$$

Table IV
REDUCTION OF CoS_2 WITH HYDROGEN

Experiment No.	Sulphur, wt.-%	Temp., °C.	H_2S/H_2	Phases Present*
Co(S)–*A*	43·7	500	11·5	$\epsilon + \phi$
	43·4	500	10·5	$\epsilon + \phi$
	43·0	500	13·1	$\epsilon + \phi$
	42·5	500	12·0	$\epsilon + \phi$
	42·1	500	10·5	$\epsilon + \phi$
	41·6	500	9·1	ϵ
	41·5	500	2·01	$\delta + \epsilon$
	41·1	500	2·03	$\delta + \epsilon$
Co(S)–*B*	48·4	369	7·6	$\epsilon + \phi$
	48·1	500	11·8	$\epsilon + \phi$
	47·7	600	22·2	$\epsilon + \phi$
	47·4	515	14·4	$\epsilon + \phi$
	47·0	495	10·2	$\epsilon + \phi$
	46·5	495	11·3	$\epsilon + \phi$
	45·5	400	6·4	$\epsilon + \phi$
	45·1	500	10·9	$\epsilon + \phi$
	44·7	500	10·9	$\epsilon + \phi$
	44·4	614	13·9	$\epsilon + (\phi)$
	44·0	607	12·2	$\epsilon + (\phi)$
	43·6	510	8·4	$\epsilon + (\phi)$
	43·3	580	11·9	ϵ
	42·8	500	9·4	ϵ
	42·4	500	8·4	ϵ
	42·0	500	7·5	ϵ
	41·7	500	4·5	ϵ
	41·4	500	2·06	$\delta + \epsilon$
	41·1	500	2·07	$\delta + \epsilon$
	41·0	405	0·61	$\gamma + \epsilon$
	40·8	405	0·54	$\gamma + \epsilon$
	40·5	462	0·90	$\gamma + \epsilon$
	40·1	510	1·90	$\delta + \epsilon$
	39·8	460	1·00	$\gamma + \epsilon$
	39·7	405	0·53	$\gamma + \epsilon$
Co(S)–*C*	48·9	400	8·2	$\epsilon + \phi$
	48·4	505	14·8	$\epsilon + \phi$
	47·8	552	16·3	$\epsilon + \phi$
	47·3	600	16·0	?
	46·6	500	12·3	$\epsilon + \phi$
	45·9	450	8·8	$\epsilon + \phi$
	45·2	400	6·0	$\epsilon + \phi$
	44·6	500	9·6	$\epsilon + (\phi)$
	44·0	500	8·9	$\epsilon + (\phi)$
	43·3	500	8·4	$\epsilon + (\phi)$
	42·6	500	6·0	ϵ
	42·0	550	6·8	ϵ
	41·3	526	6·0	$(\delta) + \epsilon$
	40·8	502	2·17	$\delta + \epsilon$
	40·1	529	3·49	$\delta + \epsilon$
	39·5	500	1·97	$\delta + \epsilon$
	32·0	475	1·39	$\delta + \epsilon$
	38·5	475	1·32	$\delta + \epsilon$
	38·3	400	0·48	$\gamma + \epsilon$
	37·8	450	0·75	$\gamma + \epsilon$
	37·4	445	0·71	$\gamma + \epsilon$
	37·0	400	0·65	$\gamma + \epsilon$
	36·6	400	0·63	$\gamma + \epsilon$
Co(S)—*D*	38·6	400	0·74	$\gamma + \epsilon$
	38·1	500	1·65	δ
	37·8	550	1·40	δ
	37·6	500	0·61	$\gamma + \delta$
	37·3	500	0·60	$\gamma + \delta$
	37·0	500	0·60	$\gamma + \delta$
	36·8	550	0·58	$\gamma + \delta$
	36·7	635	0·40	δ
	36·5	600	0·32	$\gamma + \delta$
	36·0	500	0·59	$\gamma + \delta$
	36·0	635	0·28	$\gamma + \delta$
	35·5	404	0·66	$\gamma + \epsilon$
	35·2	400	0·63	$\gamma + \epsilon$

* The phases are: $\gamma = Co_9S_8$, $\delta = CoS_{1+x}$, $\epsilon = Co_3S_4$, $\phi = CoS_2$

The curves for 700° and 800° C. show, in agreement with the work by Lundqvist and Westgren,[5] that the second sulphide phase has the composition Co_9S_8 and not Co_6S_5. This phase has only a very narrow composition range; in harmony with the results of previous investigators it was found to be stable up to about 835° C., and has therefore disappeared in the 850° C. isotherm.

The third phase, CoS_{1+x}, has its lower phase boundary at about 36 wt.-% (51 at.-%) of sulphur; *i.e.*, it does not include the stoichiometric composition. The phase boundary occurs at a somewhat higher sulphur content at 700° C. than at 800° and 1000° C.

Finally, the isotherms for 1000° and 1250° C. show the gas ratio for the molten phase from 25 to 32 wt.-% S at 1000° C. and from about 18 to 29 wt.-% S at 1250° C. A complete phase diagram for the entire binary system is shown in Fig. 7.

To clarify the phase relationships in the high-sulphur range the gas ratio was measured by means of the modified apparatus described on p. 40. The results of these experiments are given in Table IV. In Fig. 6 the gas ratios are plotted as a function of composition for constant temperatures. The sulphur pressures, expressed by the corresponding H_2S/H_2 ratios, measured by Hülsmann *et al.*[10] at higher temperatures are included.

At 500° C. three alloys (*A*, *B*, and *C*) were studied. The gas ratio for alloy *A* shows a rather sharp drop at the composition Co_3S_4, whereas the drop is more gradual for samples *B* and *C*. Alloy *A* was considerably more fine-grained than the other two, and an X-ray diffraction diagram of it showed broad and diffuse lines.* It appears that the reaction is very slow in this composition range and that, even though the gas appeared to be in equilibrium with the grain surface, the grains of alloys *B* and *C* were not in internal equilibrium. This is believed also to be the reason why the data for 400° C. are somewhat scattered.

It is evident from Fig. 6 that at 400° and 500° C. a phase with composition Co_3S_4 exists, and that this phase is relatively more stable at 400° than at 500° C. and has decomposed at some temperature between 500° and 700° C. This was confirmed by X-ray analysis. Samples of compositions between CoS and Co_3S_4 were annealed at different temperatures in evacuated and sealed silica tubes, and were then quenched. X-ray diffraction diagrams showed that whereas Co_3S_4 was stable at 600° C., it had decomposed into a mixture of CoS_2 and CoS_{1+x} at 650° C. This is in agreement with the findings by Heimbrecht, Biltz, and Meisel,[33] except that they found the decomposition temperature to be 680° C.

The curves of Fig. 6 show another interesting phenomenon. At 500° C. a second drop in the gas ratio appears at about 38 wt.-% (53 at.-%) of sulphur, which corresponds to the phase CoS_{1+x}. This drop

* This alloy had previously been used for some preliminary experiments, and had subsequently been exposed to moisture and laboratory atmosphere for about one year, whereby it was partly converted into sulphate. Before the experiments reported here, it was reduced to sulphide with hydrogen at 500° C. This treatment is probably responsible for the fine grains.

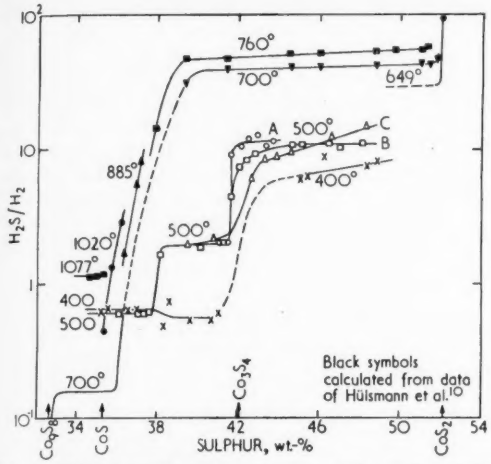

Fig. 6—Relationship between gas ratio and sulphur content for the higher cobalt sulphides

does not appear at 400° C., however; if anything, there is a slight increase in the gas ratio with decreasing sulphur content of the sulphide. The only explanation is that CoS_{1+x} is unstable at 400° C. and that the phases Co_3S_4 and Co_9S_8 are in equilibrium at this temperature. Again, X-ray analysis confirmed this conclusion. The X-ray diagrams showed, however, that the recrystallization was very slow at this temperature. The samples had to be annealed at 400° C. for a full month before lines of the recrystallization products appeared in the X-ray pattern. This demonstrates how thermodynamic methods in such a case can detect a phase change long before the X-ray analysis is able to detect any change.

It should be noted that Lundqvist and Westgren had already observed that a change took place in the X-ray pattern when CoS_{1+x} was annealed at low temperatures, and they attributed this to a polymorphic change in the monosulphide. The gas equilibrium data show clearly that this cannot be the case.

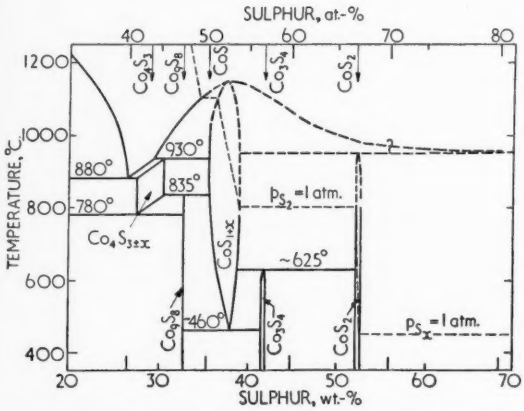

Fig. 7—Revised phase diagram for the system cobalt–sulphur

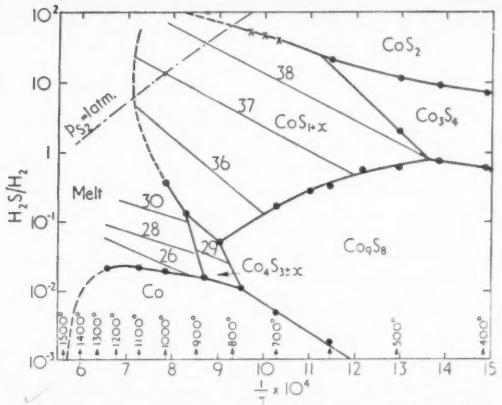

Fig. 8—Plot of H_2S/H_2 *versus* $1/T$ for the system cobalt–sulphur. Crosses are from data of Hülsmann *et al.*[10] (Compositions of alloys are in wt.-% of sulphur)

The phase relations in the entire binary system are summarized in Fig. 7, and a thermodynamic phase diagram similar to that for the iron sulphides is given in Fig. 8. The heavy lines in this diagram give the gas ratios for all two-phase equilibria in the system, and the experimental points give the average of the values measured at each temperature. For the homogeneous phases, solid and molten, the gas ratios for some constant compositions are given.

From the intersection of the various curves, and from the X-ray data, the eutectoid decomposition temperature of CoS_{1+x} is found to be about 460° C. and the peritectoid decomposition temperature of Co_3S_4 to be about 625° C.

Thermodynamic Calculations

From the curves given in Fig. 8, the Gibbs free energy ($\Delta G°$) for the reactions between the different solid phases can be obtained from the equation

$$\Delta G° = RT \ln(H_2S/H_2).$$

For $\frac{9}{8}Co + H_2S = \frac{1}{8}Co_9S_8 + H_2$ (600–775° C.):

$$\Delta G° = -18{,}039 + 8 \cdot 10T \text{ cal.} \quad \ldots\ldots\ldots\ldots (2)$$

For $\frac{4}{3}Co + H_2S = \frac{1}{3}Co_4S_{3-x} + H_2$ (775–880° C.)*:

$$\Delta G° = -9371 - 0 \cdot 16T \text{ cal.} \quad \ldots\ldots\ldots\ldots (3)$$

and for $Co_4S_{3+x} + H_2S = 4CoS_{1+x} + H_2$ (830–930° C.)*:

$$\Delta G° = -25{,}211 + 16 \cdot 90T \text{ cal.} \quad \ldots\ldots\ldots\ldots (4)$$

For the formation of CoS_{1+x} from Co_9S_8 and H_2S, the free energy cannot be expressed as a linear function of the temperature because the graph of $\log H_2S/H_2$ *vs.* $1/T$ (Fig. 8) is not a straight line. This is probably caused mainly by the change in the sulphur content of the cobalt-saturated monosulphide with changing temperature, and only to a lesser extent by the change in the specific heat of the reaction. Instead of attempting to express this relationship by a complicated arithmetical formula, the free energies

* The formulæ Co_4S_{3-x} and Co_4S_{3+x} represent the lower and upper limits of this phase. Owing to the non-stoichiometry of the phases, equations (3) and (4) are strictly stoichiometric only for H_2S and H_2.

of the reaction $Co_9S_8 + H_2S = 9CoS_{1+x} + H_2$ are listed below for four temperatures:

Temperature =	500	600	700	800° C.
ΔG° =	−640	−1730	−3490	−5740 cal....(5)

To obtain the free energy for the reaction $Co + H_2S = CoS + H_2$ it is necessary to add the free energies of the reaction steps. This can be done approximately either by adding $\frac{8}{9}$ eq. (2) and $\frac{1}{9}$ eq. (5), or by adding $\frac{3}{4}$ eq. (3) and $\frac{1}{4}$ eq. (4). Averaging the results of this procedure in the temperature range 500–1000° C. gives values which may be represented by the expression

$$\Delta G^\circ = -14{,}450 + 5{\cdot}06T \text{ cal.} \quad \ldots\ldots(6)$$

This method would be strictly correct only if the phases $Co_4S_{3\pm x}$ and CoS_{1+x} were stoichiometric phases with no solid solubility range. In the present case, however, the errors involved are rather small. A more correct procedure is described on p. 53.

For the formation of the higher sulphides the following approximate expressions apply:

For $\frac{1}{4}Co_9S_8 + H_2S = \frac{3}{4}Co_3S_4 + H_2$ (400–460° C.):

$$\Delta G^\circ = -4190 + 5{\cdot}21T \text{ cal.} \quad \ldots\ldots(7)$$

For $\frac{1}{2}Co_3S_4 + H_2S = \frac{3}{2}CoS_2 + H_2$ (400–600° C.):

$$\Delta G^\circ = -6500 + 13{\cdot}4T \text{ cal.} \quad \ldots\ldots(8)$$

and finally, from the data of Hülsmann *et al.*,[10] for $CoS_{1+x} + H_2S = CoS_2 + H_2$ (700–760° C.):

$$\Delta G^\circ = -8150 + 15{\cdot}74T \text{ cal.} \quad \ldots\ldots(9)$$

Although these linear expressions agree with the experimental values to within 100 cal., the first terms (heats of reaction) may be uncertain to about 1000 cal. and the second terms to one entropy unit.*

Owing to the width and non-stoichiometry of the monosulphide, the free energies of formation of the higher sulphides from cobalt metal cannot be calculated by simple addition of the reaction steps. They are obtained by a graphical method which is described on p. 53.

To determine the free energies of formation of the cobalt sulphides from diatomic sulphur gas (S_2), the free energy[8] of the reaction $2H_2 + S_2 = 2H_2S$, *i.e.*,

$$\Delta G^\circ = -43{,}160 + 23{\cdot}61T \text{ cal.}$$

must be added to the free energies given in the above equations. The following expressions are thus obtained:

$\frac{9}{4}Co + S_2 = \frac{1}{4}Co_9S_8$	$\Delta G^\circ = -79{,}240 + 39{\cdot}81T$ cal.
$\frac{3}{3}Co + S_2 = \frac{3}{3}Co_4S_{3-x}$	$\Delta G^\circ = -61{,}900 + 23{\cdot}29T$ cal.
$2Co + S_2 = 2CoS$	$\Delta G^\circ = -72{,}060 + 33{\cdot}73T$ cal.
$\frac{1}{2}Co_9S_8 + S_2 = \frac{3}{2}Co_3S_4$	$\Delta G^\circ = -51{,}640 + 34{\cdot}03T$ cal.
$Co_3S_4 + S_2 = 3CoS_2$	$\Delta G^\circ = -50{,}160 + 50{\cdot}41T$ cal.

The uncertainties in these expressions (about 2 k.cal. in the heat term and 2 entropy units in the entropy term) may introduce a considerable error when the values are to be used at temperatures that differ greatly from the experimental temperatures. For this purpose, the differences in specific heats will also have to be taken into consideration. Adequate specific-heat data exist only for the formation of the monosulphide, and these will be used to calculate the heat and free energy of formation of CoS at room temperature. The fact that CoS is actually unstable below 460° C. is not important in this connection.

From the data listed by Kubaschewski and Evans[9] and by Kelley,[7] the change in specific heat for the reaction $2Co + S_2 = 2CoS$ can be calculated:

$$\Delta C_p = 3{\cdot}21 - 2{\cdot}53 \times 10^{-3}T.$$

If the linear expression for the free energy (equation (6)) is regarded as valid at 1000° K., the following general expressions are obtained for the heat and free energy of reaction:

$$\Delta H^\circ = -74{,}000 + 3{\cdot}21T - 1{\cdot}27 \times 10^{-3}T^2$$
$$\Delta G^\circ = -74{,}000 - 7{\cdot}39T\log T + 1{\cdot}27 \times 10^{-3}T^2 + 56{\cdot}12T.$$

This gives, for 298° K. (25° C.):

$$\Delta H^\circ_{298^\circ\text{K.}} = -73{,}160 \text{ cal.}$$
$$\Delta G^\circ_{298^\circ\text{K.}} = -62{,}730 \text{ cal.}$$

These values differ only slightly from those obtained directly from the linear expression, *viz.*, − 72,060 and − 62,140 cal., respectively. This difference is within the limits of experimental accuracy, and therefore very little is gained by the use of the specific heats.

For the reaction $2S(rh) = S_2(gas)$, the following values apply for 298° K.[8]:

$$\Delta H^\circ_{298^\circ\text{K.}} = -31{,}020 \text{ cal.}$$
$$\Delta G^\circ_{298^\circ\text{K.}} = -19{,}360 \text{ cal.}$$

This gives for the reaction $Co + S(rh) = CoS$:

$$\Delta H^\circ_{298^\circ\text{K.}} = -21{,}070 \text{ cal.}$$
$$\Delta G^\circ_{298^\circ\text{K.}} = -21{,}700 \text{ cal.}$$

These values are regarded as correct to within 1000 cal. For comparison, existing values given in the literature are:

$\Delta H^\circ_{298^\circ\text{K.}} = -20{,}200$ (National Bureau of Standards[31])
$\Delta H^\circ_{298^\circ\text{K.}} = -22{,}300$ (Kubaschewski and Evans[9])
$\Delta G^\circ_{298^\circ\text{K.}} = -22{,}400$ „ „ „

For the other cobalt sulphides, for which no specific-heat data are known, it is regarded as safe and within the limits of experimental accuracy to apply the above linear expressions down to room temperature.

For the homogeneous phases (liquid as well as solid), the partial free energies $\Delta\mu_S$ and the partial heats of solution $\Delta\bar{H}_S$ of sulphur, referred to a mixture of equal amounts of hydrogen and hydrogen sulphide as the standard state, can be calculated from the equations:

$$\Delta\mu_S = RT\ln(H_2S/H_2)$$
$$\Delta\bar{H}_S = R\frac{d\ln(H_2S/H_2)}{d(1/T)}.$$

Owing to the rapid increase in the gas ratio with increasing sulphur content of the homogeneous phases, and to possible errors in the chemical analysis of the sulphides, the values calculated for the heat content are particularly uncertain, and may be in error by

* Combining equations (8) and (9), the decomposition temperature of Co_3S_4 is calculated to be 430° C. The X-ray diffraction diagram has shown that Co_3S_4 is stable to above 600° C. The difference may be attributed to the low accuracy of equation (9), owing to the narrow experimental temperature range. Also, it is possible that the vapour pressures determined by Hülsmann *et al.*, like those determined by Juza and Biltz for FeS_2, are rather high.

1–2 k.cal. Within these limits, the partial heat content of sulphur referred to the above standard state is as follows:

Phase	S, wt.-%	S, at.-%	$\Delta\bar{H}_S$, cal.
Liquid	26	39·3	− 13,300
	28	41·7	− 7500
	30	44·1	− 7500
$Co_4S_3 \pm x$	29	42·9	− 8500
CoS_{1+x}	36	50·9	− 16,600
	37	51·9	− 10,800
	38	53·0	− 10,500

These figures show that the partial heat of solution of sulphur decreases with increasing sulphur content of the homogeneous phases; *i.e.*, as the sulphur content increases, additional sulphur will be less strongly bound. The figures show also that the sulphur is more strongly bound in the solids than in the liquid phase of similar composition. The relationship between structure and thermodynamic properties is discussed in more detail on p. 54.

THE SYSTEM NICKEL–SULPHUR

This system is even more complicated than the cobalt–sulphur system. Earlier investigations[1] showed that in the low-sulphur range there are two phases: Ni_3S_2 (below 550° C.) and $Ni_3S_{2\pm x}$ (above 550° C.), the latter having a rather wide composition range. A third phase, of composition Ni_6S_5, is stable up to about 550° C., where it decomposes to give a mixture of Ni_3S_{2+x} and the monosulphide NiS. Bornemann[35] has suggested that a phase X exists with composition intermediate between Ni_3S_2 and Ni_6S_5, and stable only between 503° and 520° C.

Lundqvist[6] studied the system by means of X-ray diffraction diagrams, and confirmed the existence of the low-temperature form of Ni_3S_2 as well as Ni_6S_5 and NiS. The phase Ni_6S_5 was found to transform at 400° C., and at lower temperatures has a composition corresponding more closely to Ni_7S_6. Lundqvist also showed that the monosulphide transformed at about 390° C., below which temperature the hexagonal millerite modification is stable.

At higher sulphur contents the work by Lundqvist, as well as the vapour-pressure measurements by Biltz, Voigt, and Meisel,[11] proved the existence of the disulphide NiS_2. Lundqvist showed also that below some temperature between 200° and 400° C. a phase Ni_3S_4 exists.

The gas equilibrium for the reduction of the lower-nickel sulphides with hydrogen has been studied by Schenck and von der Forst.[36] They identified the high- and low-temperature forms of Ni_3S_2 as well as the Ni_6S_5 phase. However, their data, which were obtained at a limited number of temperatures, are insufficient for a complete thermodynamic description. The gas ratios determined by Jellinek and Zakowski[13] are of little value, for they did not state the compositions of their alloys.

In the present investigation, the low-sulphur range (up to 35·3 wt.-% (50·0 at.-%) of sulphur) was studied by means of the gas-circulation apparatus (Fig. 1), and the results are given in Table V. In Fig. 9 the gas ratio is plotted as a function of composition for a number of selected temperatures; the experimental points are either directly measured

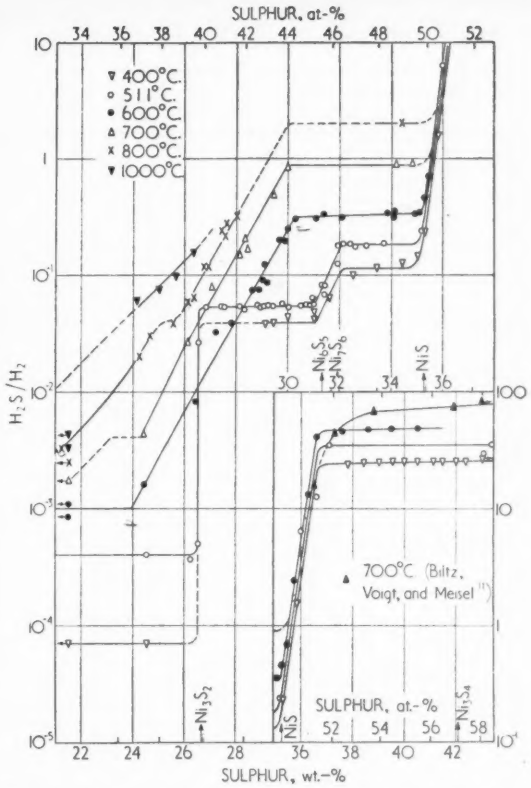

Fig. 9—Relationship between gas ratio and sulphur content for the system nickel–sulphur. (Arrowed points given at 21·5 and 43·0 wt.-% S apply to 15·0 and 44·7 wt.-% S, respectively)

values or are obtained by interpolation between closely adjacent experimental values.

The curves in Fig. 9 are in general agreement with those given by Schenck and von der Forst, but their gas ratios are about 20% higher than those obtained in the present work. This difference is probably due to thermal diffusion errors caused by gas sampling from the cold zone in the static method used by Schenck.

Phase Relations

Figure 9 shows clearly the composition and extent of the different sulphide phases. The curves for 400° and 511° C., for example, show that the phase Ni_3S_2 has a very narrow composition range. At 600° and 700° C. the phase $Ni_3S_{2\pm x}$ extends over a wide composition range from 24·0 to 30·3 wt.-% (36·6–44·3 at.-%) of sulphur.

From the variation of the gas ratios with temperature for alloys of constant compositions, the low-temperature form of Ni_3S_2 was found to be stable up to 555 ± 5° C. The high-temperature form has two eutectoids, one at 535° C. and about 24·5 wt.-% S, and the other at 525° C. and about 29·3 wt.-% S.

The third sulphide phase in the system extends over a composition range 31·0–32·1 wt.-% (45·1–46·4

Table V

REDUCTION OF NICKEL SULPHIDES WITH HYDROGEN

Experiment No.	Sulphur, wt.-%	Temp., °C.	$\frac{H_2S}{H_2} \times 10^3$	Phases Present*
Ni(S)–1a	34·3	400	12·9	$\delta + \epsilon$
1b	33·0	500	17·0	$\delta + \epsilon$
	32·1	600	31·3	$\gamma + \epsilon$
	33·4	398	11·1	$\delta + \epsilon$
Ni(S)–2	15·1	600	0·11	$\alpha + \gamma$
	15·1	815	0·35	α + liq
	15·1	1016	0·43	α + liq
	15·1	1100	0·60	α + liq
	15·1	1200	0·59	α + liq
	15·1	1400	1·37	liq
Ni(S)–3a	29·4	410	4·2	$\beta + \delta$
	29·3	435	4·8	$\beta + \delta$
	29·3	502	5·4	$\beta + \delta$
	29·2	510	5·5	$\beta + \delta$
	29·5	370	3·1	$\beta + \delta$
	29·3	548	5·1	γ
	29·2	554	5·7	γ
	28·9	629	10·3	γ
	28·2	724	19·6	γ
	28·3	710	18·1	γ
	29·1	567	7·5	γ
	29·4	390	3·9	$\beta + \delta$
Ni(S)–3b	29·1	400	3·7	$\beta + \delta$
	29·0	502	5·4	$\beta + \delta$
	28·8	612	7·9	γ
	29·0	552	5·1	γ
	29·1	548	4·9	$\beta + \gamma$
	29·0	557	5·5	γ
	28·2	687	13·8	γ
	27·6	786	21·5	γ
	27·3	880	25·5	liq
	28·5	642	10·2	γ
	28·5	650	10·7	γ
Ni(S)–4	28·8	511	5·5	$\beta + \delta$
	28·1	511	5·4	$\beta + \delta$
	27·5	511	5·3	$\beta + \delta$
	26·8	511	5·3	$\beta + \delta$
	26·5	511	2·6	β
Ni(S)–5	35·2	400	23·5	ϵ
	35·2	510	23·7	ϵ
	33·7	512	18·9	$\delta + \epsilon$
	32·1	511	18·6	$\delta + \epsilon$
	31·3	512	8·2	δ
	30·7	512	5·6	$\beta + \delta$
Ni(S)–6	31·9	509	12·3	δ
	31·4	512	6·8	δ
	31·0	514	5·7	$\beta + \delta$
	31·0	510	5·6	$\beta + \delta$
	31·0	505	5·5	$\beta + \delta$
	30·5	510	5·5	$\beta + \delta$
	30·0	512	5·3	$\beta + \delta$
	29·4	510	5·4	$\beta + \delta$
	28·9	520	5·3	$\beta + \delta$
	28·3	510	5·0	$\beta + \delta$
Ni(S)–7	26·5	511	0·05	$(\alpha) + \beta$
	26·5	550	0·12	$\beta + \gamma$
	26·4	600	0·84	γ
	26·2	680	2·2	γ
	26·2	505	0·037	$\alpha + \beta$
Ni(S)–8	35·4	522	23·4	ϵ
	34·9	600	33·7	$\gamma + \epsilon$
	33·8	600	34·0	$\gamma + \epsilon$
	31·4	600	33·3	$\gamma + \epsilon$
	29·9	600	19·3	γ
Ni(S)–9	28·6	600	7·4	γ
	27·8	600	3·9	γ
	27·2	600	3·2	γ
Ni(S)–10	31·6	544	22·2	$\delta + \epsilon$
	31·4	565	24·1	$\gamma + \epsilon$
	29·2	719	48·2	γ
	31·3	552	15·1	$\gamma + \delta$
	29·8	550	10·0	$\gamma + \delta$
	28·3	700	20·6	γ
	27·0	700	7·8	γ
	27·9	554	2·3	$\beta + \gamma$
	27·8	550	2·8	$\beta + \gamma$
	27·5	530	4·8	$\beta + \gamma$
	27·4	518	5·3	$\beta + \delta$
	27·4	506	5·3	$\beta + \delta$
Ni(S)–11	24·4	630	0·29	γ
	24·5	535	0·066	$\alpha + \beta$
	24·5	525	0·054	$\alpha + \beta$
	24·5	394	0·0061	$\alpha + \beta$
	24·5	535	0·064	$\alpha + \beta$
	24·4	585	0·139	γ
	24·4	602	0·164	γ
	24·4	720	0·629	liq + γ
	24·4	703	0·447	liq + γ
	24·3	750	1·21	liq + γ
	24·3	800	2·0	liq
Ni(S)–12	15·0	405	0·0080	$\alpha + \beta$
	15·0	395	0·0063	$\alpha + \beta$
	15·0	450	0·0218	$\alpha + \beta$
	15·0	600	0·085	$\alpha + \gamma$
	15·0	632	0·100	$\alpha + \gamma$
	15·0	700	0·174	α + liq
	15·0	830	0·242	α + liq
	15·0	995	0·314	α + liq
	15·0	1090	0·457	α + liq
	15·0	895		α + liq
	15·0	645	0·325	α + liq + γ
			0·149	
Ni(S)–13a	31·6	400	6·3	δ
	31·4	510	8·1	δ
	31·3	525	8·7	δ
	31·2	550	10·6	$\gamma + \delta$
	30·1	595	24·3	γ
	31·5	400	5·3	δ
13b	31·0	400	4·8	$(\beta) + \delta$
	30·9	511	6·4	$(\beta) + \delta$
	30·6	543	9·4	$\gamma + \delta$
	30·1	560	14·8	$\gamma + \delta$
	30·2	558	13·6	$\gamma + \delta$
	29·7	594	20·0	γ
	29·6	608	21·6	γ
	30·9	525	6·8	$(\beta) + \delta$
	30·9	503	6·4	$(\beta) + \delta$
Ni(S)–14	35·0	402	14·4	ϵ
	35·0	446	15·7	$\delta + \epsilon$
	34·1	595	30·3	$\gamma + \epsilon$
	34·7	518	20·7	$\delta + \epsilon$
	31·8	706	91·6	$\gamma + \epsilon$
	30·0	700	85·9	$\gamma + \epsilon$
	29·4	701	49·1	γ
	30·1	559	13·6	γ
	30·7	530	7·2	$\gamma + \delta$
	30·9	522	5·4	$\beta + \gamma + \delta$
	30·8	500	5·8	$\beta + \delta$
	31·0	404	4·2	$\beta + \delta$

* The phases are: $\alpha = Ni$, $\beta = Ni_3S_2$ (low-temperature form), $\gamma = Ni_3S_{2\pm x}$ (high-temperature form), $\delta = Ni_6S_{5+x}$, $\epsilon = NiS_{1+x}$
Doubtful phases are given in parentheses

Table V (*Contd.*)

REDUCTION OF NICKEL SULPHIDES WITH HYDROGEN

Experiment No.	Sulphur, wt.-%	Temp., ° C.	$\frac{H_2S}{H_2} \times 10^3$	Phases Present*
Ni(S)–15	29·9	400	4·3	$\beta + \delta$
	29·7	514	5·8	$\beta + \delta$
	29·3	560	9·8	γ
	29·0	606	12·9	γ
	28·3	700	20·7	γ
	27·7	796	27·6	γ
	27·6	808	29·1	γ
	27·7	816	28·4	liq
	27·6	806	29·1	γ
	27·4	799	24·1	γ
Ni(S)–16a	32·5	414	9·9	$\delta + (\epsilon)$
	32·5	400	9·9	$\delta + (\epsilon)$
	31·7	522	18·8	$\delta + (\epsilon)$
	32·0	506	17·4	$\delta + (\epsilon)$
	31·2	595	30·3	$\gamma + \epsilon$
16b	29·8	595	20·6	γ
	29·8	600	20·7	γ
16c	29·2	610	8·7	γ
	29·2	602	8·5	γ
Ni(S)–17a	27·8	810	34·2	(liq + γ)
	27·9	806	33·2	(liq + γ)
17b	27·0	796	10·4	(liq + γ)
	26·9	798	11·4	(liq + γ)
	26·7	804	13·6	(liq + γ)
	26·9	799	11·7	(liq + γ)
17c	26·3	808	6·6	(liq + γ)
	26·3	796	6·3	(liq + γ)
	26·4	789	5·6	(liq + γ)
Ni(S)–18a	26·7	806	12·4	(liq + γ)
	26·7	800	12·0	(liq + γ)
	26·4	900	14·6	liq
	26·3	1002	15·4	liq
	26·9	795	10·8	(liq + γ)
	26·1	800	5·9	(liq + γ)
	25·8	900	8·1	liq
	25·6	1000	9·4	liq
	26·0	806	6·0	(liq + γ)
18b	25·5	800	3·8	liq
	25·2	900	5·7	liq
	25·0	1000	7·4	liq
18c	24·1	1000	6·0	liq
	24·4	900	4·3	liq
	24·6	800	3·0	liq

* The phases are: α = Ni, $\beta = Ni_3S_2$ (low-temperature form), $\gamma = Ni_3S_{2\pm x}$ (high-temperature form), $\delta = Ni_6S_{5+x}$, $\epsilon = NiS_{1+x}$
Doubtful phases are given in parentheses

Table VI

REDUCTION OF NiS_2 WITH HYDROGEN

Experiment No.	Sulphur, wt.-%	Temp., ° C.	H_2S/H_2	Phases Present*
Ni(S)–*A*	44·7	400	26·2	$\epsilon + \phi$
	43·8	400	26·5	$\epsilon + \phi$
	43·4	500	35·0	$\epsilon + \phi$
	43·1	500	28·0	$\epsilon + \phi$
	42·4	400	24·1	$\epsilon + \phi$
	42·0	400	24·8	$\epsilon + \phi$
	41·5	400	24·8	$\epsilon + \phi$
	41·1	400	24·8	$\epsilon + \phi$
	40·5	400	25·0	$\epsilon + \phi$
	40·0	400	24·9	$\epsilon + \phi$
	39·5	400	25·2	$\epsilon + \phi$
	39·0	400	24·3	$\epsilon + \phi$
	38·4	400	24·1	$\epsilon + \phi$
	37·8	400	23·7	$\epsilon + \phi$
	37·1	510	34·8	$\epsilon + \phi$
	36·6	510	12·6	ϵ
	36·0	510	6·3	ϵ
	35·8	400	1·55	ϵ
Ni(S)–*B*	40·5	585	48·0	$\epsilon + \phi$
	39·5	600	47·6	$\epsilon + \phi$
	38·6	600	48·0	$\epsilon + \phi$
	37·6	600	46·0	$\epsilon + \phi$
	36·6	600	41·0	$\epsilon + (\phi)$
	36·3	600	13·0	ϵ
	35·8	600	2·46	ϵ
	35·5	600	0·69	ϵ
Ni(S)–*C*	35·3	600	0·47	ϵ
	35·1	600	0·35	$\gamma + \epsilon$
	34·8	700	0·92	$\gamma + \epsilon$
	34·4	800	2·11	$\gamma + \epsilon$
	34·2	700	0·89	$\gamma + \epsilon$
	34·1	600	0·35	$\gamma + \epsilon$

* The phases are: $\gamma = Ni_3S_{2+x}$, $\epsilon = NiS_{1+x}$, $\phi = NiS_2$

at.-%) of sulphur, and thus includes the stoichiometric compositions Ni_6S_5 as well as Ni_7S_6. This phase was found to be stable up to 560 + 5° C. Too few experiments were made below 400° C. to detect the phase transformation and composition change which Lundqvist found for this phase.

The curve for 511° C. shows clearly that no phase exists at this temperature between the compositions Ni_3S_2 and Ni_6S_5. The phase *X* which Bornemann[35] assumed to exist between 503° and 520° C. is therefore non-existent; nor did the present work give any indication of the existence of the non-variant line at 503° C. which Bornemann found by thermal analysis.

At 800–1000° C. some data were obtained for the melt with up to 29 wt.-% S. The curves for these temperatures show the same general trend as was found for the iron and cobalt sulphide melts.

The monosulphide NiS_{1+x} has its lower composition limit at about 35·1 wt.-% (49·8 at.-%) S, *i.e.*, very close to the stoichiometric composition.

For alloys with higher sulphur contents the gas ratio was determined with the modified apparatus described on p. 40. The data obtained for these sulphides with 35·5–44·2 wt.-% S are given in Table VI. Figure 9 (lower right) shows the gas ratio as a function of composition for selected temperatures. As with the cobalt sulphides, these curves are supplemented with gas ratios derived from the vapour-pressure measurements by Biltz, Voigt, and Meisel.[11] At 400° and 510° C. the monosulphide extends from 35·1 to about 36·6 wt.-% (49·8–51·4 at.-%) S; that is, the composition range of the monosulphide is considerably narrower than in the iron and cobalt sulphur systems. The width is less than that given by Biltz *et al.* and agrees more closely with the width given by Lundqvist (*i.e.*, about 1 at.-%).

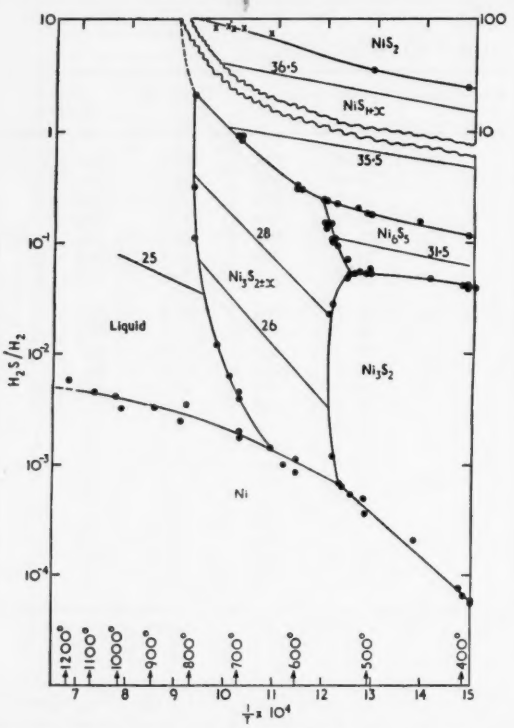

Fig. 10—Plot of H_2S/H_2 *versus* $1/T$ for the system nickel–sulphur. (Compositions of alloys are in wt.-% of sulphur)

Figure 9 shows that no phase of composition Ni_3S_4 exists at 400° C. Owing to the low rates of reaction no measurements were made below 400° C., at which temperature, according to Lundqvist, such a phase exists.

A thermodynamic phase diagram of the binary system is shown in Fig. 10. As with the iron and cobalt sulphur systems, only those experimental points corresponding to two-phase equilibrium are given. A few curves are also given which show the gas ratio for a number of constant compositions within the homogeneous phases. Owing to the rapid change in the gas ratio with changing composition of the solid solutions, these curves, and particularly their slopes, are sensitive to errors in the chemical analysis of the alloys.

The phase relations in this system are summarized in Fig. 11, supplemented with data obtained by other investigators.

Thermodynamic Calculations

From the curves given in Fig. 10, the following linear expressions for the free energies may be calculated from the equation $\Delta G^\circ = RT\ln(H_2S/H_2)$:

$\frac{3}{2}Ni + H_2S = \frac{1}{2}Ni_3S_2 + H_2$ (400–535° C.)
$\Delta G^\circ = -18{,}040 + 7{\cdot}70T$ cal. .....(10)

$2Ni_3S_2 + H_2S = Ni_6S_5 + H_2$ (400–525° C.)
$\Delta G^\circ = -3050 - 1{\cdot}85T$ cal. .....(11)

$Ni_6S_5 + H_2S = 6NiS + H_2$ (400–560° C.)
$\Delta G^\circ = -5220 + 3{\cdot}46T$ cal. .....(12)

$\frac{3}{2}Ni + H_2S = \frac{1}{2}Ni_3S_2 - x + H_2$ (535–650° C.)
$\Delta G^\circ = -11{,}950 - 3{\cdot}23T$ cal. .....(13)

$Ni_3S_2 + x + H_2S = 3NiS + H_2$ (560–810° C.)
$\Delta G^\circ = -16{,}600 + 16{\cdot}8T$ cal. .....(14)

$NiS_1 + x + H_2S = NiS_2 + H_2$ (400–800° C.)
$\Delta G^\circ = -4700 + 13{\cdot}34T$ cal. .....(15)

Owing to the non-stoichiometry of the phases involved, equations (13), (14), and (15) are strictly stoichiometric with respect to the gases only. All these expressions agree with the experimental values to within 100 cal., but since they are determined for rather narrow temperature ranges the accuracy of the individual terms may be considerably lower. This applies also to equation (15), which is based on the gas ratios obtained in the present work combined with the vapour-pressure data obtained by Biltz, Voigt, and Meisel.

As the phase Ni_6S_5 and the low-temperature form of Ni_3S_2 have rather narrow composition ranges, the free energies of formation of Ni_6S_5 and NiS from nickel metal may be calculated by simple addition of the reaction steps.

For $\frac{6}{5}Ni + H_2S = \frac{1}{5}Ni_6S_5 + H_2 = \frac{4}{5}$eq.(10) + $\frac{1}{5}$eq. (11),

$\Delta G^\circ = -15{,}040 + 5{\cdot}79T$ cal. .....(16)

For $Ni + H_2S = NiS + H_2 = \frac{2}{3}$eq.(10) + $\frac{1}{6}$eq.(11) + $\frac{1}{6}$eq.(12),

$\Delta G^\circ = -13{,}400 + 5{\cdot}40T$ cal. .....(17)

If the free-energy expressions given above are combined with the free energy for the reaction $2H_2 + S_2 = 2H_2S$, *viz.*,

$\Delta G^\circ = -43{,}160 + 23{\cdot}61T$ cal.,[8]

the free energy of formation of the nickel sulphides from diatomic sulphur gas may be calculated.

For the reaction $2Ni + S_2 = 2NiS$,

$\Delta G^\circ = -69{,}960 + 34{\cdot}41T$ cal. .....(18)

The NiS transforms at 396° C. in the low-temperature form, millerite. From their thermal analysis data Biltz *et al.*[11] estimated the heat of this transformation to be about 7 cal./g., or 630 cal./mol. Nickel, on the

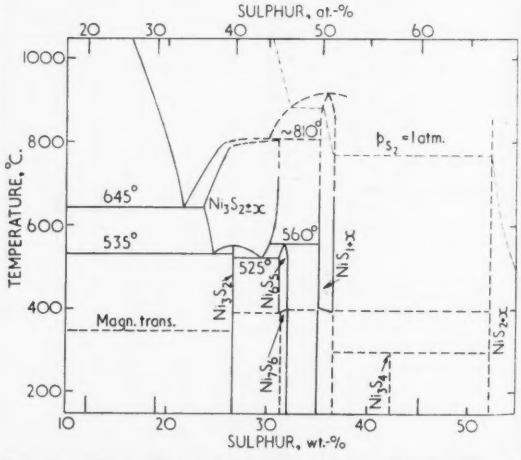

Fig. 11—Phase diagram for the system nickel–sulphur. Uncertain phase boundaries are drawn with broken lines

other hand, has a magnetic transformation point at 358° C., with a heat of transformation of 140 cal.[9] However, this is more than offset by the higher specific heat of nickel sulphide; the integrated value of ΔC_p for the reaction $Ni + \frac{1}{2}S_2 = NiS$ between 25° and 400° C. is about 250 cal.[9] Below 396° C. the free energy of formation of 2NiS (millerite) from Ni + S_2(gas) may then be given by

$$\Delta G^\circ = -71{,}320 + 36{\cdot}46T \text{ cal.} \quad \ldots\ldots(19)$$

Finally, for the reaction Ni + S(rh) = NiS (at 25° C.):

$$\Delta H^\circ_{298^\circ\text{K.}} = -20{,}200 \text{ cal.}$$
$$\Delta G^\circ_{298^\circ\text{K.}} = -20{,}600 \text{ cal.}$$

These figures may be incorrect to about 1 k.cal., owing to the many uncertainties in their determination. For comparison, existing values given in the literature are:

$\Delta H^\circ_{298^\circ\text{K.}} = -17{,}500$ cal. (National Bureau of Standards[31])
$\Delta H^\circ_{298^\circ\text{K.}} = -20{,}400$ cal. (Kubaschewski and Evans[9])
$\Delta G^\circ_{298^\circ\text{K.}} = -20{,}700$ cal. ,, ,, ,,

The free energies of formation of the other nickel sulphides are calculated graphically in the next section.

The Total Free Energy of Sulphide Formation

It is difficult to express arithmetically the free energy of formation of a sulphide phase that has a wide composition range, particularly when the composition limits vary with the temperature. For this purpose a graph of the total free energy of the binary mixture as a function of its composition is preferable. (This point was made and discussed in the recent paper by Richardson and Jeffes.[8]) Graphs for the iron, cobalt, and nickel sulphides are shown in Fig. 12, all drawn for a temperature of 1000° K.

The total free energy of formation of a sulphide mixture of composition A_mS_n (A = metal, $m + n = 1$) is given by the expression:

$$\Delta G^\circ = m\Delta\mu_A + n\Delta\mu_S$$

where $\Delta\mu_A$ and $\Delta\mu_S$ denote the differences between the chemical potentials of metal and sulphur in the mixture and in the standard states chosen. For the formation of the sulphides from metal and hydrogen sulphide, a gas mixture with H_2S/H_2 equal to unity may be chosen as a standard state for sulphur. Referred to this standard state, $\Delta\mu_S = RT\ln(H_2S/H_2)$.

Since a tangent to the curve of free-energy *vs.* n, if extended to $n = 1$ (100% S), will intersect the ordinate for this composition at a value which corresponds to $\Delta\mu_S$, the free-energy curves were constructed in the following way:

From the origin (A = 100%, $\Delta G^\circ = 0$), a ruler is laid across the graph to the right-hand scale (S = 100%) and through the value for $\Delta\mu_S = RT\ln(H_2S/H_2)$ corresponding to equilibrium between the metal phase and the first sulphide phase. A straight line is drawn until the lower composition limit of the first sulphide phase is reached. Within the one-phase region the slope of the ruler is changed continuously so that it always intersects the right-hand scale of the graph at the value for $\Delta\mu_S$ that applies to the composition at which the ruler is a tangent to the curve. Through the next two-phase region the ruler is kept fixed, intersecting the right-hand scale at the value for $\Delta\mu_S$ that corresponds to the new two-phase equilibrium, and so on. Values for $\Delta\mu_A$ may then be obtained from the intersection of the tangent ruler with the left-hand scale (A = 100%).

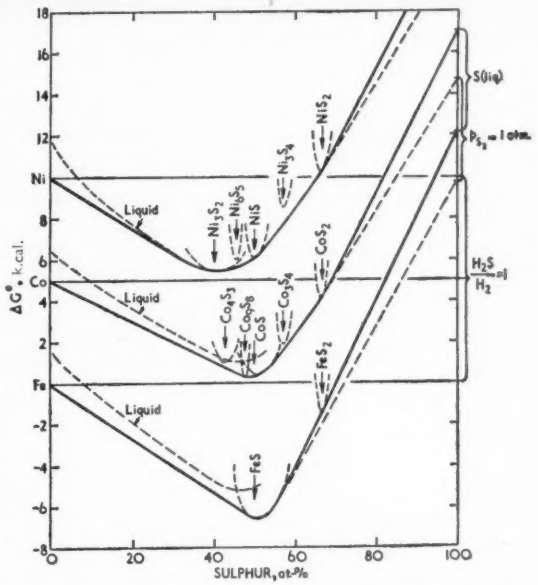

Fig. 12—Total free energy of formation of the iron, cobalt, and nickel sulphides at 1000° K. (727° C.) from solid metals and hydrogen sulphide. The ordinate scale applies to the system Fe–S; the curves for the Co–S and Ni–S systems are displaced by 5 and 10 k.cal., respectively

This procedure is simpler than a graphical integration of the Gibbs–Duhem equation and is, in this particular case, equally precise.

At sulphur contents higher than that of the disulphide, $\Delta\mu_S$ will correspond to that of liquid sulphur, *i.e.*, about + 12,250 cal. at 1000° K. In Fig. 12 is also drawn the tangent corresponding to $p_{S_2} = 1$ atm., for which $\Delta\mu_S = +9775$ cal. at 1000° K.[8]

Dotted lines are drawn in Fig. 12 for the phases which are unstable at that particular composition or temperature. Thus the curves for the molten phases are constructed from the heats of fusion of the different metals and monosulphides and from the shape of the liquidus curves, as well as from gas equilibrium values for the intermediate compositions, extrapolated to 1000° K.

These curves apply for a total of one mole of A + S. Therefore, to obtain the free energy of formation of one mole of a certain compound, the values from the curves have to be multiplied by the number of atoms per mole. The values given in Table VII (for formation from metal and hydrogen sulphide) were obtained in this way. To obtain the free energy of formation from metal and S_2 vapour, 9775 cal. must be added to these values for each atom of sulphur in the compound.

Similar total free-energy curves were constructed for several other temperatures above and below 1000° K., whereby the free energy of formation was

Table VII

MOLAR FREE ENERGIES, ENTROPIES, AND HEATS OF FORMATION OF IRON, COBALT, AND NICKEL SULPHIDES AT 1000 °K. (727° C.)

Reference states: Solid metals, hydrogen sulphide, and hydrogen at 1 atm.

Compound	$\Delta G°$, cal.*	$\Delta S°$, cal./° C.	ΔH, cal.*	$S_{1000° K.}$†
FeS	−13,350	− 0·82	−14,170	35·7
FeS_2	− 3900	−30·0	−33,900	27·0
Co_4S_3	−28,500	+ 0·5	−28,000	125·2
Co_9S_8	−79,500	−64·8	−144,300	241·4
CoS	− 9350	− 5·1	−14,450	31·2
Co_2S_4	−25,200	−28·5	−53,700	100·9
CoS_2	− 2500	−23·0	−25,500	33·8
Ni_3S_2 (low-temperature form)	−20,700	−15·4	−36,100	74·2
Ni_3S_2 (high-temperature form)	−22,900	− 2·5	−25,400	87·1
Ni_6S_5	−46,000	−29·0	−75,000	170·7
NiS	− 8000	− 5·4	−13,400	31·3
NiS_2	+ 580	−19·0	−18,400	38·2

* To obtain the free energy and heat of formation from S_2 (gas), — 9775 and — 21,580 cal., respectively, must be added for each atom of sulphur in the compound

† The entropies of the reference states at 1000° K. have been calculated from their entropies at 298° K. and their specific heats between 298° and 1000° K. as given by Kubaschewski and Evans.[9] The following values for $S_{1000° K.}$ were used: Fe = 16·0, Co = 15·8, Ni = 16·2, H_2S = 60·2, H_2 = 39·7. The accuracy of the calculated entropy values is estimated to one entropy unit per atom of sulphur in the compound. For the iron sulphides the values may be compared with those obtained from heat-capacity data by Coughlin[40] and Kubaschewski and Evans. These give for FeS, $S_{1000° K.}$ = 36·1, and for FeS_2, $S_{1000° K.}$ = 33·6 entropy units

obtained as a function of temperature. These values, together with those calculated arithmetically in the previous sections, are plotted in Fig. 13. In accordance with the practice adopted by Richardson and Jeffes[8] and others, the standard state for sulphur is here chosen to be one mole of S_2 gas, and the free energies all refer to an amount of sulphide which contains two atoms of sulphur.

In addition to the free energy of formation, these curves also give the entropy of formation ΔS, which is equal to $-d\Delta G/dT$. The heat of formation $\Delta H = \Delta G + T\Delta S$ can then be calculated. These values are included in Table VII.

For sulphides that undergo phase transition, the break in the curve at the transition point corresponds to the entropy of transition. Thus, for the transition of Ni_3S_2 at 550° C. the entropy of transition is found to be equal to 13 entropy units, which corresponds to a heat of transition of about 11,000 cal.

DISCUSSION

The Solid Phases

The curves in Figs. 12 and 13 demonstrate clearly how the stability of the different sulphides decreases with increasing atomic number of the metal. It will also be seen that the composition of the most stable sulphides shifts to a lower sulphur content as the atomic number of the metal is increased.

In the system iron–sulphur the most stable composition corresponds to slightly more than 50 at.-% S; in the cobalt–sulphur system it is 47 at.-% S, and in the nickel–sulphur system it is 40 at.-% S. Copper, the next metal in the periodic table, forms the very stable compound Cu_2S, so that the system copper–sulphur will have its minimum free energy at 33·3 at.-% S. This shift is in harmony with the rules of the chemistry of ions in aqueous solutions, that the lower valencies become increasingly more stable in the sequence iron–copper. Apart from this analogy, it is not easy to see why the equilibrium diagrams of the three binary systems differ as they do. In particular, the compositions Co_9S_8 and Ni_6S_5 differ drastically from what would be expected on the basis of classical valency conceptions.

The occurrence of the different sulphide phases is a result of the chemical binding forces, which again are determined by the composition of the compound in question and the characteristic properties of the participating elements. The stable atomic arrangements are those which give the most satisfactory answer to the requirements of the chemical forces. The presence of a particular phase is not necessarily a result of very great stability of the phase itself; it may equally well result from the relatively low stability of the neighbouring, competing phases. Figure 12 shows that if a compound Fe_9S_8 of the same stability as Co_9S_8 had existed, it would not appear in the equilibrium diagram because of the much greater stability of FeS_{1+x}. The number of possible compounds may be very large, but only those for which the free-energy curve extends below the common tangent of the two neighbouring phases are stable.

The free energy of a compound is determined by two factors: the heat of formation, and the entropy of formation. These are connected by the expression $\Delta G = \Delta H - T\Delta S$. On increasing the order in the crystal lattice the entropy of formation will decrease; *i.e.*, the term $-T\Delta S$ in the free-energy expression will increase. The stable structural arrangement will be that for which the free energy has its minimum. At any temperature above absolute zero this arrangement will be somewhat more disordered than that corresponding to the lowest heat of formation. The higher the temperature the more the entropy term will dominate and the more disordered the structure will be. Crystal structures which correspond to the lowest heat of formation will usually have rather complex atomic arrangements and will offer few possibilities for disorder. They will therefore be preferred at low temperatures, whereas at higher temperatures they will be overtaken by simpler structures with less order and higher entropy, even though these have a more positive heat of formation. This relationship is easily seen for the cobalt and nickel sulphides, where the low-temperature phases Co_9S_8 and Ni_6S_5 have rather complicated crystal structures and low entropies, whereas the high-temperature phases CoS_{1+x} and NiS_{1+x} have the simple NiAs structure and higher entropies. The highest entropy per atom is found for the high-temperature phases $Co_4S_{3\pm x}$ and $Ni_3S_{2\pm x}$, which indicates that these phases have rather loose and disordered structures. Unfortunately, the structures of these phases have not yet been determined.

In Table VII are summarized the free energies, heats of formation, and entropies of the different iron,

cobalt, and nickel sulphides, at 1000° K. All these values apply for the formation from the respective metals and hydrogen sulphide. After the entropies of the components at 1000° K. have been added, the entropies of the sulphides, $S_{1000°\,K.}$, are obtained (shown in the last column). This eliminates the slight differences in entropy of the three pure metals and makes it possible to compare the different sulphides directly.

When the values for the three monosulphides are compared it will be noticed that the heats of formation are about equal, whereas the entropy has a considerably more positive value for FeS than for CoS and NiS. Therefore, the difference between the stability of the three compounds is not primarily a result of different binding strength, but rather of a higher degree of structural disorder in the iron sulphide than in the other two compounds. On cooling, FeS transforms into a low-temperature superstructure that has an entropy which corresponds more closely to those of CoS and NiS.

Although the higher entropy of FeS may be caused partly by a higher vibrational frequency of the atoms, it seems more likely to be a result of a larger structural disorder. It is known that compounds with NiAs structure may have variable compositions which are connected with structural defects. A deficiency in metal atoms corresponds to vacant lattice positions, as in FeS_{1+x}, whereas an excess of metal atoms may be present in interstitial lattice positions, as in $FeSb_{1-x}$.[37] The present data indicate that even at a stoichiometric composition iron sulphide has a considerable degree of disorder, which may be caused by an equal number of lattice vacancies and interstitial iron atoms.

In a recent paper, Anderson[38] discussed the relationship between intrinsic disorder and the thermodynamics of compounds of this type. He showed that the change in the fugacity of one component with changing composition of the homogeneous phase increases as the degree of intrinsic disorder decreases, and consequently that the width of the homogeneous range will be lowest for the compound with the lowest intrinsic disorder, *i.e.*, lowest entropy. This is in agreement with the observation that the composition range of FeS_{1+x} is wider than those of NiS_{1+x} and CoS_{1+x}.

For larger deviations from stoichiometry, Anderson showed that interaction between adjacent vacancies or adjacent interstitial atoms will somewhat modify this relationship. When the interaction between interstitial metal atoms is rather high it may cause the stability range of the compound to fall entirely outside the stoichiometric composition, as is found in the present case for CoS_{1+x}.

As Anderson himself pointed out, his formulæ may be regarded as approximations and suffer from errors of oversimplification. For this reason, and because of the low accuracy of the thermodynamic data obtained for the homogeneous phases, it does not seem pertinent at present to apply Anderson's formulæ quantitatively. From a qualitative viewpoint, however, the differences in entropy and width for the three different monosulphides may be regarded as resulting from decreasing intrinsic disorder as well as from decreasing interaction between the defects, in the sequence FeS to NiS.

Whereas the entropies of the monosulphides decrease in the sequence FeS to NiS, the entropies of the disulphides increase from FeS_2 through CoS_2 to NiS_2. The negative heat of formation, referred to hydrogen sulphide, decreases in the same sequence. This means that the binding forces decrease and the intrinsic disorder, and probably the width of the composition range, increase in the same sequence. This last point may be supported by the vapour-pressure data obtained by Biltz and his co-workers,[4, 10, 11] which show that the composition range of, for example, NiS_2 possibly extends to $NiS_{3\cdot5}$; part of this effect, however, may be due to non-attainment of equilibrium during their experiments.

The factors that determine the stability of the lower sulphides of cobalt and nickel are not clearly understood. An understanding may be sought in the factors that determine the stability and crystal structure of alloy phases (*e.g.*, the Hume-Rothery phases). In these phases, rather complicated structures are stabilized at compositions which have certain ratios of valency electrons to atoms, because these structures permit the valency electrons to occupy low-energy levels.

In this connection, attention is drawn to the recent investigation by Lundqvist[39] of the ternary system iron–nickel–sulphur. Lundqvist showed that sulphides containing equal amounts of iron and nickel show great resemblance to the cobalt sulphides. Thus, the phase $(Fe,Ni)_9S_8$ (the natural mineral pentlandite) has the same crystal structure as Co_9S_8. This structure is, therefore, stabilized primarily by the electron/atom ratio. Moreover, Ni_3S_4 is able to replace almost 50% of its nickel content with iron. Most unexpectedly, however, the disulphides FeS_2 and NiS_2 do not form extensive solid solutions with each other—solid solutions that might have represented an analogy to CoS_2.

The Liquid Phases

Although rather few data were obtained for the liquid phases, they will give, if combined with earlier data, a general picture of the sulphur activity as a function of sulphur concentration in the melt.

For the iron–sulphur melts, the low-temperature range was studied by Sherman, Elvander, and Chipman,[29] and the range of intermediate sulphur content (up to 30 wt.-% S) by Maurer, Hammer, and Möbius.[25] In the low-sulphur range the sulphur activity shows a pronounced negative deviation from Henry's law and remains at intermediate sulphur contents (*i.e.*, 10–20% S), almost independent of the composition. At higher sulphur contents the sulphur activity shows a rapid increase, which reaches a maximum around the stoichiometric composition. This behaviour seems to be general for most metal–sulphur systems. In some cases, such as Ag–Ag_2S,[1, 17] and Cu–Cu_2S,[1] the melt separates into two co-existing liquid phases. In the case of Fe–FeS the melt is at the point of separation into two phases, whereas in the case of Co–CoS and Ni–NiS the tendency towards liquid separation is less pronounced.

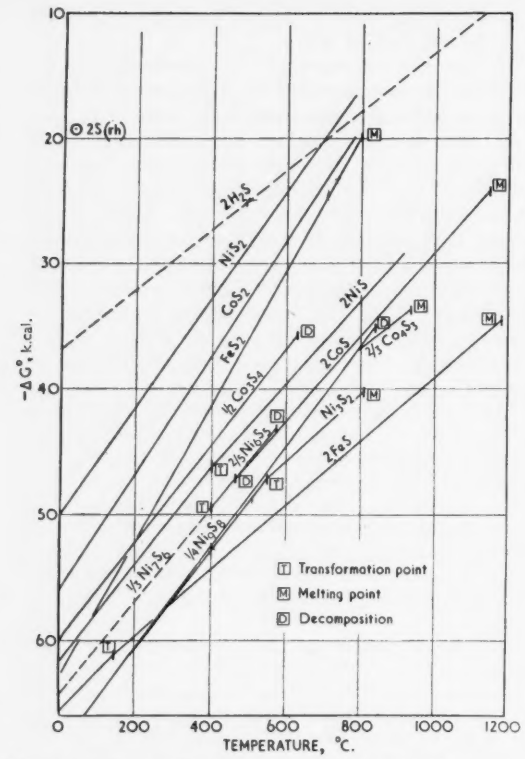

Fig. 13—Free energy of formation of closely stoichiometric sulphides from solid metals and S_2 gas

The factors that may be responsible for this behaviour are:

(i) Partial ionization of the metal and sulphur particles; *e.g.*, according to the equation $Fe + S \rightleftharpoons Fe^{2+} + S^{2-}$. This reduces the concentration of 'neutral' sulphur atoms, and consequently the sulphur activity, in the melt.

(ii) Electrostatic interaction between neighbouring ionized particles, which results in the formation of short-range clusters of closely stoichiometric composition even in melts of lower sulphur contents. This results in a tendency towards liquid separation.

The author hopes to return to this interesting subject, as well as to the question of sulphur activity in ternary and more complex melts, in another paper.

SUMMARY

The decomposition pressures of the various iron, cobalt, and nickel sulphides have been determined as functions of the composition and temperature of the sulphides. In the low-sulphur range the decomposition pressures were determined by means of the reaction with hydrogen to form hydrogen sulphide. The apparatus shown in Fig. 1 was used for gas ratios H_2S/H_2 from 10^{-5} to unity. For higher gas ratios a modified apparatus was used. For the decomposition of pyrite the sulphur pressure was measured with a dew-point apparatus. The data obtained are summarized in Tables I to VI. From the variation of the decomposition pressures with the composition of the sulphides, the presence and extent of the various sulphide phases were determined. Thermodynamic constants for the decomposition process were calculated from the variation of the decomposition pressure with temperature for all two-phase equilibria. By arithmetical or graphical addition of the constants for the different decomposition steps, thermodynamic constants for the formation of the different sulphides from the elements were obtained. These are shown in Fig. 13 and Table VII. The results are discussed with emphasis on their connection with the structure of the different sulphide phases and the nature of the chemical binding forces.

Acknowledgments

The experimental work reported in this paper was carried out while the author was connected with the Institute for the Study of Metals, University of Chicago, U.S.A. The author wishes to express his gratitude to the Director of that Institute, Dr. Cyril S. Smith, for the experimental facilities, and to all members of the Institute staff for inspiring discussions. Most of the metal sulphides were analysed at the Institute, for which thanks are due to the Head of the Analytical Laboratory, Dr. N. H. Nachtrieb.

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Correspondence on the Paper—

ACTIVITIES OF CONSTITUENTS OF IRON AND STEELMAKING SLAGS: Part I—IRON OXIDE*

By E. T. Turkdogan and J. Pearson

Dr. **W. A. Fischer** and Dr. **H. vom Ende** (Max-Planck Institute, Düsseldorf) wrote: According to Turkdogan and Pearson, the oxygen contents we found[1] in iron melts under silica-saturated slags are lower than those determined by other workers. Figure *A* gives our results, together with those of Körber and Oelson[2] and Fetters and Chipman,[3] and also results we obtained in carbon monoxide atmospheres, which Turkdogan and Pearson have overlooked. All the points are distributed uniformly about a curve for which we have given the equation

$$\log[O]_{SiO_2} = -\frac{3920}{T} + 1{\cdot}08 \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

From this and the Taylor-Chipman equation[4] for the temperature-dependence of the oxygen content of liquid iron in equilibrium with practically pure FeO slags, *viz.*,

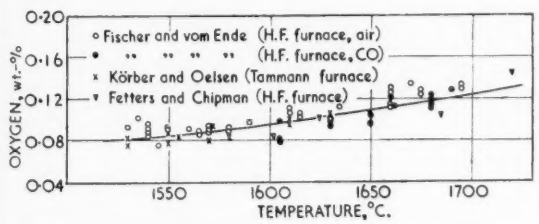

Fig. A—Influence of temperature on the oxygen contents of iron melts under silica-saturated ferrous oxide slags

$$\log[O]_{FeO} = -\frac{6320}{T} + 2{\cdot}73 \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

the temperature-dependence of the activity of FeO in silica-saturated slags may be calculated:

$$\log a_{FeO} = \frac{2400}{T} - 1{\cdot}65 \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

It follows from this that the activity of FeO decreases with increasing temperature. Since Turkdogan and Pearson have also used equation (2) for calculating a_{FeO} but found activity to increase with temperature, they must have used another expression for equation (1) which gives higher oxygen contents and, in particular, a more pronounced increase of oxygen content with temperature. What experimental results did Turkdogan and Pearson use for this?

In Fig. *B*, which corresponds to Fig. 1*a* of Turkdogan and Pearson's paper, are plotted the activity values we obtained for equilibrium in air and carbon monoxide. The values under carbon monoxide show the same molar concentration of FeO at saturation as that assumed by Turkdogan and Pearson, but they again assume for this concentration a higher activity, corresponding to their higher equilibrium oxygen content. From the results of Schuhmann and Ensio,[5] an activity of 0·377 at 1600° C. was extrapolated by the use of the equation $\log a_{FeO} = \frac{300}{T} - 0{\cdot}590$; this value agrees well with the group of points plotted.

* *J. Iron Steel Inst.*, 1953, vol. 173, pp. 217–223.

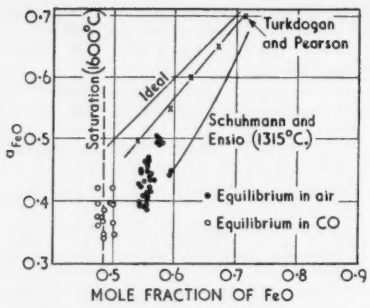

Fig. B—Dependence of a_{FeO} of silica-saturated slags on the molar concentration of FeO

We have also found[1] that the concentration of silica at saturation in air varied between 34·4% and 40·4%, depending on temperature, in good agreement with the work of Michal and Schuhmann,[6] who obtained 38% of SiO_2 at 1600° C. at $\log(p_{CO_2}/p_{CO}) = 2·0$. This proves satisfactorily that equilibrium existed between metal, slag, and gas, contrary to the statement by Turkdogan and Pearson.

With basic slags, Turkdogan and Pearson also assume higher values of a_{FeO} than those obtained by us and by Fetters and Chipman.[3] For temperatures between 1550° and 1640° C. the latter authors determined a_{FeO} as 0·32–0·44 (melts *E*12 and *E*15), which agrees well with our values of 0·32–0·49 at 1540–1700° C. For slags of this concentration, Turkdogan and Pearson assume activities of 0·5–0·6 (*see* Fig. 4). It would be interesting to know from what investigations Turkdogan and Pearson took their oxygen values.

AUTHORS' REPLY

Dr. **Turkdogan** and Dr. **Pearson** wrote in reply: We have used no expression similar to equation (1), nor did we state explicitly that the activity of ferrous oxide in silica-saturated slags increased with temperature. Indeed, we did not criticize the results of Fischer and vom Ende on the grounds that they found activity in silica-saturated slags to *decrease* with temperature.

We were concerned to show why we did not use their experimental results in our considerations. Our statement that the oxygen contents in the metal found by Fischer and vom Ende were lower than those obtained by previous workers under *similar* slags was perhaps not well expressed. The method we adopted was to select, from the work of the authors quoted, slags which could be considered as essentially iron-oxide–silica melts. From the determined oxygen contents of the metals in contact therewith, we obtained the activity of ferrous oxide in the slag. We calculated the total iron content of the slag to FeO and then plotted a_{FeO} against N_{FeO}; this gave Fig. 1*a*. When the same procedure was applied

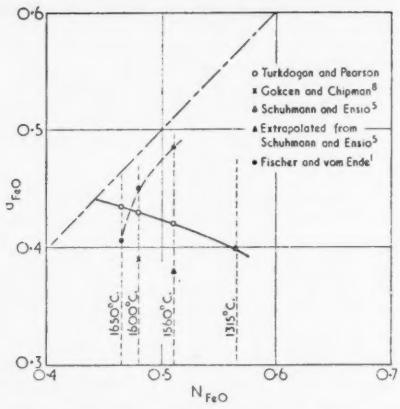

Fig. C—Effect of temperature on a_{FeO} in silica-saturated ferrous oxide slags

to the results of Fischer and vom Ende, the oxygen contents and thus the activities of FeO were found to be low in comparison with those plotted in Fig. 1*a*. We attributed this to the fact that, although the oxygen contents of the iron determined by Fischer and vom Ende were correct (and the manner in which they fit Fig. 4 of their paper confirms this), the slag they analysed was not the same as that which was in contact with the iron during the experiments. We suggested why this should be so and based our argument on the fact that their calculated values of Fe_2O_3 were as high as 6·55%. Silica-saturated slags in equilibrium with liquid iron contain only traces of Fe_2O_3.

Having established the position of the lines in Fig. 1*a* to the best of our ability, we terminated each line at a point corresponding to silica saturation and then drew in the ' silica-saturated ' line. It is this which indicates that the activity of ferrous oxide in silica-saturated slags increases with temperature. Rey[7] has indicated that in FeO–SiO_2 slags more acid than the orthosilicate the activity of FeO should show an increase with temperature.

We will admit that the effect of temperature on a_{FeO} in silica-saturated ferrous oxide slags is still open to doubt. As may be seen from the attached Fig. *C*, the results of three independent sets of workers[1, 5, 8] are not in good agreement. The curve we have drawn might be considered to be an average of existing results.

With regard to more complex slags, we do not consider it surprising that examples can be found which are at variance with our iso-activity diagram. This was constructed on the basis of our Fig. 3, which in turn was based on results for slags falling into the groups noted. Any few results which did not fit in with the general tendency were neglected. Our sources of data were given in references 1–7 in the original paper.

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Reaction Equilibria Between Metal and Slag in Acid and Basic Open-Hearth Steelmaking

By E. T. Turkdogan, Ph.D., M.Met., and J. Pearson, Ph.D., M.Sc., F.R.I.C.

SYNOPSIS

A study has been made of the extent of equilibrium between metal and slag with respect to reactions involving manganese, phosphorus, ferrous oxide, and carbon. Manganese and phosphorus contents of open-hearth steel, calculated from slag composition, are in good agreement with those found analytically. This indicates that equilibrium distribution of these two elements is readily attained.

Ferrous oxide distribution between metal and slag reaches equilibrium only at very low carbon contents. When the carbon content is high the oxygen potential of the slag is much higher than that corresponding to equilibrium with the carbon; the oxygen content of the metal is then intermediate between that in equilibrium with the slag and that in equilibrium with the carbon. This is attributed to the slowness of the reaction between carbon and oxygen. Equilibrium with respect to oxygen exists only at the slag–metal interface.

Fluoride in slag appears to lower the activity coefficient of dissolved phosphorus pentoxide and should therefore have a beneficial influence on the removal of phosphorus. 823

THE control of metal–slag reactions in steelmaking would be facilitated if it could be shown that equilibrium exists between the two phases during refining and is re-established rapidly after any additions. The distribution of any material could then be directly assessed from a knowledge gained from laboratory experiments in which equilibrium had been deliberately established. Obviously it would not be feasible to cover experimentally all the variations that occur in steelmaking, but experiments should permit the equilibrium ratio of the concentrations of reactants and resultants to be defined in such a way as to be applicable to a wide range of conditions.

This equilibrium ratio is usually thought of as a constant, but in fact it should be defined so that its value, at a given temperature, is independent of the conditions under which equilibrium exists. This is best done by first specifying the reacting species in the simplest manner and then determining the equilibrium constant, as a function of temperature, in a system in which it can be shown that activities are equal or equivalent to concentrations. The constant so obtained will be valid in all circumstances, provided that the activities of the reacting species, and not their concentrations, are employed.

In previous papers[1, 2, 3] the equilibrium constants of the manganese and phosphorus reactions have been evaluated and methods have been given for determining the activities of ferrous oxide, manganous oxide, and phosphorus pentoxide in slags. It is thus possible to calculate, from open-hearth slag analyses, the equilibrium content of manganese, phosphorus, and oxygen in steel and, by comparison with determined values, to assess the extent of approach to equilibrium.

DISTRIBUTION OF MANGANESE BETWEEN METAL AND SLAG

The equilibrium constant of the reaction

$$\underline{\text{Mn}} + \text{FeO (in slag)} = \text{MnO (in slag)} + \underline{\text{Fe}} \quad \ldots\ldots(1)$$

is given by[2]

$$\log K_{\text{Mn}} = \log \frac{(a_{\text{MnO}})}{(a_{\text{FeO}})\,[\text{Mn}\,\%]} = \frac{7406}{T} - 3{\cdot}436 \quad \ldots\ldots(1a)$$

The activities of MnO and FeO in a number of open-hearth slags have been assessed by the methods described previously.[1, 2] The compositions of the slags were taken from publications by Vajragupta[4] (laboratory melts), Stark and Chelishchev,[5] Tenenbaum and Brown[6] (basic open-hearth), and Herasymenko[7] (acid open-hearth), and from unpublished results obtained by B.I.S.R.A. staff.* The equilibrium manganese contents of the steels were calculated by means of equation (1*a*) and were plotted against determined manganese (Fig. 1). The standard deviation of calculated from determined manganese content is $\pm 0{\cdot}036\%$, and, since the calculated results exhibit no tendency to be consistently higher or lower than those found in practice, it must be concluded that the transfer of manganese between steel and slag is a relatively fast process and that the equilibrium is re-established within a short period after any additions (of ore, lime, etc.) or any change in temperature.

Paper CP/10/14 of the Chemistry Department of the British Iron and Steel Research Association, received 27th May, 1953.

Dr. Pearson is Head of the Chemistry Department and Dr. Turkdogan is Head of the Physical Chemistry Section of the Chemistry Department of the Association.

* From trial basic open-hearth heats carried out in collaboration with Messrs. John Summers and Sons Ltd., Shotton.

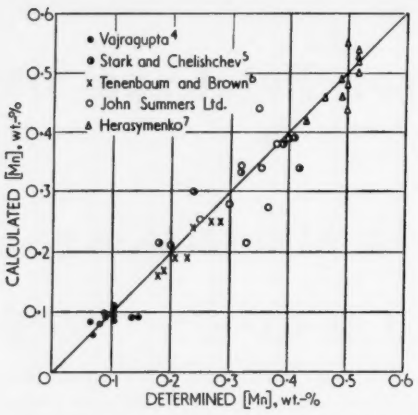

Fig. 1—Comparison between calculated and determined manganese content of steel

Witten[8] came to the same conclusion from other considerations. It should be noted that equality of calculated and determined values of [Mn%] is independent of the carbon content of the metal; Vajragupta's experiments were conducted with carbon-free metal, whereas the carbon contents of the acid and basic open-hearth heats varied from 0·1 to 1·0%.

DISTRIBUTION OF PHOSPHORUS BETWEEN METAL AND SLAG

Phosphorus is removed from steel by oxidation, and the equilibrium constant of the reaction

$$\underline{2P}(1\%) + \underline{5O}(1\%) = P_2O_5 \text{ (liquid)} \ldots\ldots\ldots (2)$$

has been calculated[3] to be

$$\log K_P^O = \frac{36{,}850}{T} - 29{\cdot}07 \ldots\ldots\ldots (2a)$$

It was found that equation (2*a*) is valid only if the oxygen content is determined on essentially carbon-free metal or is calculated from the activity of ferrous oxide in the slag, *i.e.*, $[O\%] = L_{FeO} \cdot a_{FeO}$. From the known value of L_{FeO},[9] the equilibrium constant of the reaction

$$\underline{2P}(1\%) + 5FeO \text{ (in slag)} = P_2O_5 \text{ (in slag)} \ldots (2b)$$

may be written

$$\log K_P = \log \frac{(a_{P_2O_5})}{(a_{FeO})^5 [P\%]^2} = \frac{5250}{T} - 15{\cdot}4 \ldots\ldots (2c)$$

By using equations (2*a*) and (2*c*) it has been shown[3] that the effect of slag composition and temperature on the activity of phosphorus pentoxide can be expressed as:

$$\log \gamma_{P_2O_5} = -1{\cdot}12 \Sigma A_i N_i - \frac{42{,}000}{T} + 23{\cdot}58 \ldots (2d)$$

where

$$\gamma_{P_2O_5} = a_{P_2O_5}/N_{P_2O_5} \ldots\ldots\ldots (2e)$$

$$\Sigma A_i N_i = 22N_{CaO} + 15N_{MgO} + 13N_{MnO} + 12N_{FeO} - 2N_{SiO_2} \ldots\ldots\ldots (2f)$$

and N = mole fraction of oxide constituent.

Equation (2*c*) was obtained from laboratory results and from open-hearth metal and slag analyses at tap,* and has been used to calculate, from refining slag compositions, the phosphorus contents of some basic open-hearth melts at periods before tap. The values obtained were plotted against those determined analytically (Fig. 2).

The standard deviation of calculated from determined phosphorus content is $\pm 0{\cdot}005\%$, and it thus appears that the transfer of phosphorus, also, between metal and slag quickly reaches a state of equilibrium under steelmaking conditions, independent of the carbon content. Witten[8] also found this to be true.

Slags Containing Fluoride

Basic open-hearth slags frequently contain fluoride, added usually as fluorspar, and it has been suggested[10] that this fluoride makes dephosphorizing more effective by lowering the activity of phosphate in the slag. On the assumption that equilibrium also exists when the slags contain fluoride, the data of Herasymenko and Speight[11] can be used to determine the effect of fluoride on the activity coefficient of phosphorus pentoxide. The value of $\gamma_{P_2O_5}$ was calculated with the aid of equation (2*c*). In assessing the activity of ferrous oxide, due allowance was made for the presence of fluoride; from previous considerations[1] it was known that fluoride raised the activity of FeO by an amount Δa_{FeO} proportional to the fluoride concentration (*see* Fig. 3*a*). The value of $\gamma_{P_2O_5}$ so obtained was inserted into equation (2*d*) to give the effective value of $\Sigma A_i N_i$. This was found to be higher than that calculated from the slag composition by equation (2*f*). The difference $\Delta\Sigma A_i N_i$, which is attributed to the effect of fluoride in lowering the activity coefficient of P_2O_5, is dependent on the fluoride content of the slag, as shown in Fig. 3*b*. The term 'ion fraction' is used in this diagram to signify that fluoride ions are considered as separate slag constituents; the number thereof in 100 g. of slag is calculated by dividing the percentage content by the atomic weight of fluorine and adding the result to the number of moles of CaO, MgO, etc., to give the total number of 'moles' per 100 g. of slag. The calcium content of any added fluorspar is reckoned in with the CaO, as is usual in reporting slag analyses.

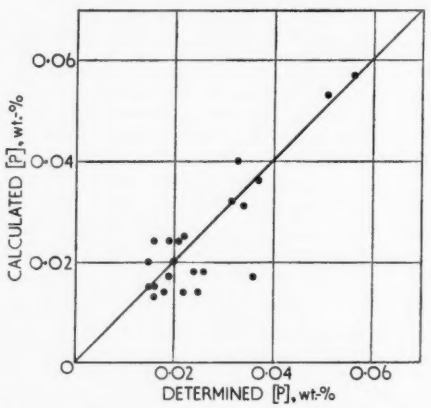

Fig. 2—Comparison between calculated and determined phosphorus content of steel

* At John Summers and Sons Ltd. (*q.v.*).

The slope of the line in Fig. 3*b* (*i.e.*, 31) is the factor A_i for fluoride ions. For slags containing fluoride, equation (2*f*) now takes the form

$$A_iN_i = 22N_{CaO} + 15N_{MgO} + 13N_{MnO} + 12N_{FeO} + 31N_F - 2N_{SiO_2} \quad \ldots\ldots(2g)$$

DISTRIBUTION OF OXYGEN OR FERROUS OXIDE BETWEEN METAL AND SLAG

The distribution of oxygen or ferrous oxide between metal and slag may be represented, in its simplest form, as

$$\underline{O} + \underline{Fe} = FeO \text{ (in slag)} \quad \ldots\ldots(3)$$

the equilibrium constant of which is given by[9]

$$\log K_O = \frac{\log a_{FeO}}{[O\%]} = \frac{6320}{T} - 2{\cdot}734 \quad \ldots\ldots (3a)$$

The activity of FeO in slags can be derived from the oxygen content of pure iron in equilibrium therewith, and the results can be illustrated on an isoactivity diagram.[1] The reverse procedure, *i.e.*, calculating oxygen contents of metal from slag composition, has been carried out for some acid and basic open-hearth heats, and the results are plotted against determined oxygen contents in Fig. 4. The carbon content of the molten steel was 0·1–1·0%, and it is clear that under these conditions the oxygen content of the bulk of the metal, at least, is not in equilibrium with the slag; *i.e.*, the oxygen potential of the slag is always higher than that of the steel.

REMOVAL OF CARBON FROM STEEL DURING REFINING

The oxidation of carbon in steel may be represented by the reaction

$$\underline{C} + \underline{O} = CO \text{ (gas)} \quad \ldots\ldots(4)$$

the equilibrium constant of which is given by[12]

$$\log K_C = \log \frac{p_{CO}}{a_C \cdot a_O} = \frac{1860}{T} + 1{\cdot}643 \quad \ldots\ldots(4a)$$

In basic and acid open-hearth steelmaking, the carbon–oxygen relationship is not the same as that

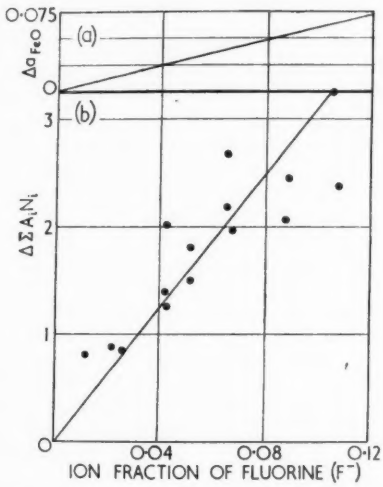

Fig. 3—Effect of fluoride on activities of (*a*) ferrous oxide, (*b*) phosphorus pentoxide

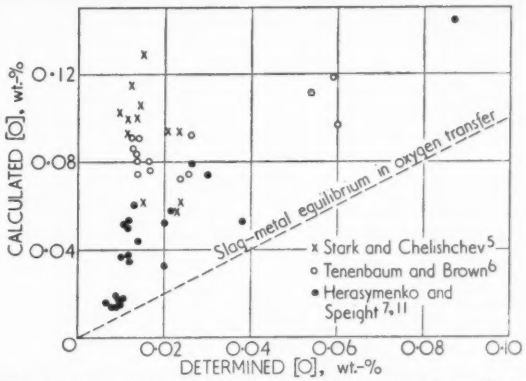

Fig. 4—Comparison between calculated and determined oxygen content of steel

indicated by equation (4*a*), even when allowance is made for the effect of carbon concentration on its own activity[13,14] and on that of oxygen.[13] This is indicated in Fig. 5, in which [O%] is plotted against [C%] for a number of acid and basic open-hearth melts. All experimental points, at a temperature of 1600 ± 20° C., lie in a band (*A*) above the Vacher–Hamilton isothermal for 1600° C. This isothermal gives the ideal relationship between [O%] and [C%] at a pressure of 1 atm. of carbon monoxide.

Figure 5 also includes plots of [O%], calculated from a wide range of slag compositions, against the carbon content of the steel. The oxygen contents calculated from the activity of ferrous oxide in the slag are obviously much higher than those actually present in the bulk of the metal, and are distributed at random within a band (*B*). When the carbon content is low, *i.e.*, below about 0·05%, the calculated and analytical oxygen contents are in close agreement.

DISCUSSION

Figures 1, 2, and 4 indicate that during steel refining there exists an equilibrium between metal and slag with respect to the distribution of manganese and phosphorus, independent of the carbon content of the steel, but that equilibrium with respect to oxygen distribution exists only at very low carbon contents. Manganese and phosphorus differ from carbon in that their oxidation products, MnO and P_2O_5, are soluble in slag; indeed, it might be said that the oxidation of these alloying elements is possible under steelmaking conditions only because the oxides do dissolve in the slag and exist at low activity. In other words, MnO and P_2O_5 are not formed in the bulk of the metal but only at the slag–metal interface. The metal there, although constantly being changed, should maintain the same oxygen potential as the slag and, provided that the rate of oxidation of manganese and phosphorus is fairly rapid, equilibrium with respect to their partition should be established.

Carbon, however, is oxidized to a gas, carbon monoxide, which is not soluble in the slag, and oxidation of carbon can and does take place away from the slag–metal interface. The fact that the carbon content of an open-hearth bath is usually higher than that in equilibrium with the oxygen

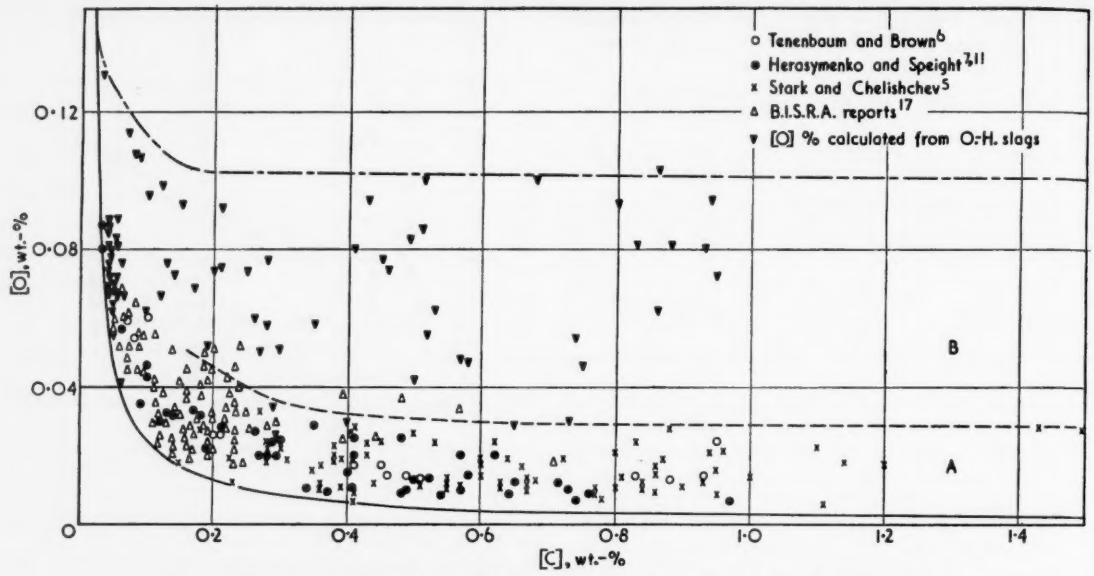

Fig. 5—Carbon–oxygen relationship in acid and basic open-hearth processes

potential of the metal at the interface, as calculated from the slag composition, indicates that the carbon–oxygen reaction is slow. The most likely reason for this has been given by Goodeve,[15] who states that "The carbon monoxide molecules formed in this reaction may suffer dissociation again or join together to form a bubble of gas. Owing to the facts that this growth requires a rapid succession of collisions with fresh CO molecules and that a liquid metal will resist with great energy the formation of a hole large enough to form the nucleus of a gas bubble, this second stage of the reaction is likely to be slow." The fact that removal of carbon from iron is controlled by a nucleation process is indicated by the sudden gas evolution which may set in when a bath is stirred.

It has been held that the reason for the non-obedience of the Vacher–Hamilton isothermal in open-hearth refining is that the effect of the energy required to form bubbles of gas is equivalent to changing the pressure of CO in equation (4) from 1 atm. to about 2 atm. If an average curve is drawn through the points in band (*A*) in Fig. 5, the apparent CO pressure will be equivalent to 1·5–8 atm., the higher figure holding at high carbon contents. It is hardly likely that the energy to form CO bubbles will vary in this way; it seems more probable that the actual extent of approach to true equilibrium will depend on the presence of chance factors that favour the nucleation of gas bubbles.

Although dissolved carbon is unable to reduce the oxygen potential of the bulk of the metal to a value that corresponds to the Vacher–Hamilton curve, the reaction is sufficiently fast to prevent the slag from raising the oxygen potentials of the bulk to a value in equilibrium with the FeO in the slag. In other words, the slag is tending to raise the oxygen potential of the metal to a level indicated by the band (*B*) in Fig. 5, and the carbon is tending to reduce it to a value indicated by the lower line in Fig. 5; the net result is that the oxygen content of the steel lies within band (*A*).

It is therefore evident that the carbon content of steel is not an indicator of the oxygen potential that exists in the bulk of the metal nor of that existing at the slag–metal interface, where other reactions take place. It is for this reason that phosphorus can be removed in the presence of relatively high proportions of carbon if the slag employed is of the correct type, *i.e.*, one with a high iron-oxide activity and in which phosphorus pentoxide is held at low activity. Similar considerations are expected to apply in the case of basic Bessemer melts, and Lellep[16] has shown that, with a molten calcium ferrite slag and bottom-blown oxygen, phosphorus can be reduced from 1·5% to obout 0·05% while the carbon drops only from 3% to 1·5%.

CONCLUSIONS

There is good agreement between the manganese and phosphorus contents of open-hearth steel and those calculated from the slag composition. This indicates that their distribution between metal and slag readily reaches equilibrium under steelmaking conditions and that the oxidation of manganese and phosphorus is a fast reaction.

The oxygen content of metal, calculated from the slag composition, is much higher than that determined in practice, when the carbon content is greater than about 0·05%. This is attributed to the slowness of the oxidation of carbon, which cannot therefore reduce the oxygen content of the bulk of the metal to that in equilibrium with itself, but which nevertheless maintains it at a lower level than would be in equilibrium with the slag. The slag is, of course, constantly undergoing oxidation by the furnace atmosphere or by ore additions.

It follows from the above that it is at the slag–metal interface only that the oxygen potential of the

steel can be the same as that of the slag, unless there is insufficient carbon in solution to prevent the bulk oxygen content from rising.

Fluoride ions in slag lower the activity coefficient of phosphorus pentoxide and increase the activity of ferrous oxide, and thus exert a favourable effect on dephosphorizing.

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Absorptiometric Determination of Cobalt in Iron and Steel

By the Methods of Analysis Committee

SYNOPSIS

The procedure developed for the determination of cobalt and put forward in the Appendix is essentially based upon the method of Haywood and Wood. It differs in that the boiling period to destroy interfering ions is eliminated, other light filters are preferred, and reagent additions are adjusted to compensate for the presence of certain alloying elements. 806

COBALT in steels is usually determined gravimetrically by precipitation of the element with nitroso-β-naphthol and subsequent ignition to cobaltic oxide under carefully controlled conditions. Preliminary separation of the iron group is a necessary factor of the procedure.

The method is tedious and sometimes gives low results owing to the adsorption of cobalt by the hydrolysed iron group, even after a double precipitation, and also by tungstic acid when present. The need for a more accurate and convenient method led to the examination of absorptiometric procedures, among which the method of Haywood and Wood* appeared to be promising. This, unlike many of the others considered, does not involve an iron separation, but relies upon the development of a red cobalt complex in neutral or buffered solution by the addition of nitroso-R-salt (sodium 1-nitroso-2-naphthol-3: 6-disulphonate). Tungsten is retained in solution by phosphoric acid. This method had already been used in a modified form to determine very small quantities of cobalt, and its operation on a wider scale was considered to merit detailed study.

This investigation was carried out by the Physico-Chemical Methods of Analysis Sub-Committee.†

Paper MG/D/50/53 of the Methods of Analysis Committee of the Metallurgy (General) Division of the British Iron and Steel Research Association, received 17th July, 1953.

* F. W. Haywood and A. A. R. Wood, *Journal of the Society of Chemical Industry*, 1943, vol. 62, pp. 37–39.

EXPERIMENTAL WORK

Range of the Method

This has been confined to amounts of cobalt not exceeding about 12%, but there is no reason why the

† The constitution of the Sub-Committee at 30.9.52 was: Mr. H. G. SHORT (*Chairman*), N.P.L.; Mr. E. DYKE (replaced Mr. B. BAGSHAWE, 1.4.52), Brown-Firth Research Laboratories; Mr. D. BELL, Colvilles Ltd.; Mr. H. COX, Metropolitan-Vickers Electrical Co., Ltd.; Mr. F. E. EBORALL, Geo. Senior and Sons, Ltd.; Mr. L. E. GARDNER, Edgar Allen and Co., Ltd.; Mr. C. H. R. GENTRY, Philips Electrical Ltd.; Mr. H. GROOM, Bragg Laboratory (N.O.I.D.); Mr. S. HARRISON, Kayser Ellison and Co., Ltd.; Mr. G. PADGET, United Steel Companies, Ltd.; Miss R. PRESSER, B.C.I.R.A.; Miss L. E. SPARROW, G.K.N. Research Laboratories; and Mr. J. O. LAY (*Secretary*), B.I.S.R.A.

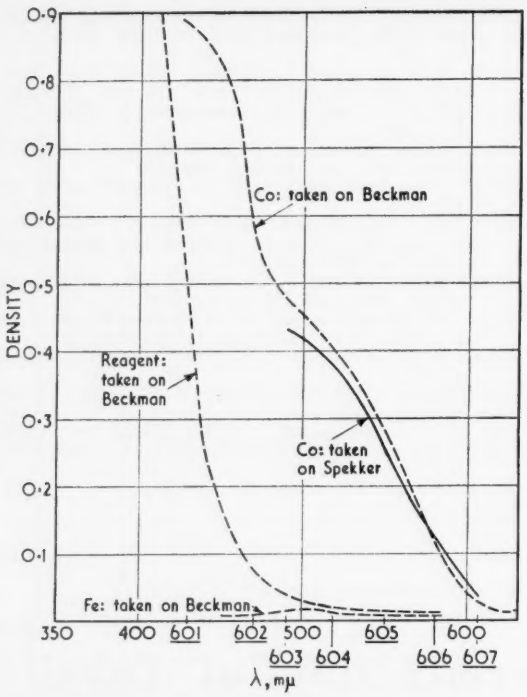


Fig. 1—Density/wavelength curves for cobalt, present as a complex with nitroso-R-salt. Cobalt concentration 2 mg./l., iron concentration 500 mg./l. Method of preparation as Appendix, using 1-cm. cell and tungsten lamp. Figures underlined refer to Ilford spectrum filters

method should not operate at a higher level with suitable modification.

Choice of Filter

For convenient application of the method to high-cobalt steels great sensitivity is not required. The amount of reagent used may also vary within wide limits and, to reduce the absorption due to the excess, Ilford 606 filters have been used (Fig. 1).

The Reagent

Pure nitroso-R-salt is a yellow powder that readily dissolves in water to give a green solution. The green colour is easily destroyed by the addition of mineral acids, giving a yellow solution. About 3·5 ml. of the reagent solution specified is required for every 1·0% of cobalt (0·005 g.) present in the original sample, except where large quantities of nickel or copper are present.

The yellow colour gives only a slight absorption when measured with Ilford 606 filters: 50 ml. of reagent solution give an absorptiometer reading of 0·061 (= 0·048% of Co) when a 4-cm. cell is used.

In practice, however, such an amount of free reagent would never occur, the bulk of the reagent being consumed by the formation of the cobalt complex.

The Cobalt Colour Complex

This is readily produced in a steel solution by the addition of sodium acetate and the reagent. Any interfering complexes produced by other elements with nitroso-R-salt are destroyed by the addition of 5 ml. of nitric acid (sp. gr. 1·42).

The colour thus produced is stable for a long time; it is unaffected by large variations in the sodium acetate addition and is only very slightly affected by large excesses of nitric acid.

INTERFERING ELEMENTS

In the method put forward by Haywood and Wood, the colours are produced, nitric acid (sp. gr. 1·42) is added, and the solution is boiled for 1–2 min. to destroy complexes of other metals and excess reagent.

In practice the boiling time is very critical and can appreciably affect the accuracy of the method. It has been shown that the alloying elements usually present in steel do not cause interference under the specified conditions, and boiling has therefore been omitted.

Iron

The iron complex is readily destroyed by nitric acid. A very slight decrease in sensitivity occurs with increase in iron content, and steps should be taken to ensure that the calibration curve is prepared in the presence of iron equivalent to that present in the samples for analysis. The following figures show the effect of iron upon the calibration:

Iron Present, g.	Cobalt per 100 Absorptiometer Drum Divisions (0·5-cm. cell)
0·00	6·40
0·15	6·35
0·35	6·20
0·50	6·20

Vanadium and Tungsten

The method will tolerate at least 10% (0·05 g.) of vanadium, and no interference has been noted with 20% of tungsten.

Nickel

Although nickel does not form any coloured complex, when it is present this element does consume reagent. This has been considered when specifying the quantity of reagent for each cell size, and in practice there is enough excess reagent to tolerate about 9–10% (0·045–0·050 g.) of nickel in the original sample, although 5% is stipulated in the method.

For the examination of alloys that consist primarily of nickel, calibration under working conditions is recommended, using a suitable excess of reagent to compensate for the nickel present. In practice, 1% of nickel (0·005 g.) in the original sample, equivalent to 0·0005 g. in the fraction, will consume about 0·8 ml. of 0·3% reagent. It was found, for instance, from tests designed to investigate the point, that in a sample containing 50% of nickel 50 ml. of reagent solution were required for full development of the colour from 2·4% of cobalt. With 20% of nickel, 25 ml. were required under the same conditions.

Copper

The interference of copper is similar to that of nickel in that it consumes reagent but does not produce a highly coloured complex. It is, however, more serious, since the amount of reagent required under method conditions is about three times that

Table I
ANALYSES OF STEELS USED

Steel	C, %	Cr, %	W, %	V, %	Mo, %	Ni, %	Co, %
MGS 50	0·9	4·6	6·7	1·4	4·2	...	0·7
,, 62	2·2	18·8	2·0	...	...	2·15	3·0
,, 98	0·8	4·5	18·0	1·5	1·0	...	10·5
,, 160	1·4	13·0	...	...	0·7	2·0	4·0
,, 173	1·3	12·0	...	0·8	...	...	1·0
,, 180	0·8	4·3	19·0	1·0	0·8	...	5·5
,, 181	...	...	...	...	...	40·0	0·3

required for nickel. For instance, a sample containing 5% of copper required 16 ml. of reagent solution for full development of the colour from 1% of cobalt; with 10% of copper, 26 ml. were required. An addition of an extra 2 ml. of reagent solution for each 1% of copper present in the sample (0·0005 g. of copper in the test solution) must be made.

The following figures show that the actual colour interference due to copper at 5% level when using a 2-cm. cell is equal to a drum difference reading of 0·005, the equivalent of less than 0·01% of cobalt:

	0·5-g. Sample, 0% Co, 606 Filter, 2-cm. Cell		
Test No.	Cu, %	Reagent, ml.	Drum Difference Reading
1	nil	30	0·032
2	1·0	30	0·032
3	2·0	30	0·032
4	5·0	30	0·037
5	10·0	30	0·050

APPLICATION OF THE METHOD

Having modified the method in accordance with the results of the foregoing investigation, the procedure (*see* Appendix) was applied to the series of alloy steels shown in Table I. Table II shows the results obtained on these steels.

CONCLUSIONS

A well-known method for the absorptiometric determination of cobalt has been examined with care, and, with minor modifications, (*see* the Appendix), satisfactory results have been obtained on a wide variety of alloy steels. The revised method will be recommended for adoption as a British Standard.

APPENDIX

Recommended Method

Procedure

Dissolve 0·5 g. (Note 1) of sample in 20 ml. of phosphoric–sulphuric acid mixture (3 : 3 : 14) by digestion on a hot plate (Note 2). When solution of the sample is complete, oxidize dropwise with nitric acid (sp. gr. 1·42) and evaporate to fumes. Allow to cool, add 50 ml. of water, and gradually bring to a boil. Cool and dilute to exactly 100 ml. (Note 3).

Pipette two 10-ml. fractions (*a* and *b*) into 100-ml. graduated flasks and continue as described below. It is recommended that all additions be made from burettes or pipettes.

(*a*) *Test Solution*—Add 0·3% nitroso-R-salt as indicated in Note 4 and mix; add 10 ml. of sodium acetate solution (50%), mix well, and stand for 5 min. at room temperature. Add 5 ml. of nitric acid (sp. gr. 1·42) and stand for a further 5 min. at room temperature. Dilute to 100 ml. with water.

(*b*) *Compensating Solution*—Add 10 ml. of sodium acetate solution (50%) and 5 ml. of nitric acid (sp. gr. 1·42), and dilute to 100 ml. with water.

Measure the absorption of each solution using the range 560–600 mμ. For the Hilger photo-electric absorptiometer, suitable conditions are:

Mercury-vapour lamp
Water setting 1·00
Ilford 606 filters together with H503 filters.

Table II
COBALT CONTENTS OF TEST STEELS, %

Analyst	MGS 50	MGS 62	MGS 98	MGS 160	MGS 173	MGS 180	MGS 181
1	0·68	2·88	...	...	...	5·45	0·32
2	0·65	2·85	...	...	...	5·40	0·29
3	0·68	2·88	10·56	3·98	1·08	5·44	0·34
4	0·69	2·89	10·46	3·97	1·05	5·53	0·29
5	0·66	2·86	10·51	3·88	1·04	5·40	0·28
6	0·69	2·95	10·62	4·08	1·01	5·48	0·35
7	0·68	2·87	10·67	3·99	1·05	5·46	0·30
8	0·68	2·89	10·84	4·04	1·02	5·45	0·29
9	0·70	2·96	10·58	3·93	1·02	5·41	...
10	0·65	2·88	10·40	3·88	1·01	5·50	0·325
11	0·665	2·85	10·90	4·00	1·03	5·45	0·315
Average	0·675	2·89	10·62	3·97	1·035	5·48	0·31
Range	0·05	0·11	0·50	0·20	0·07	0·13	0·07

The cell used for calibrating the instrument should be used for all subsequent measurements. In the case of breakage of the cell or failure of the mercury-vapour lamp, the instrument must be recalibrated.

4-cm. cell	range	0–0·8% of Co
2-cm. ,,	,,	0–1·6% of Co
1-cm. ,,	,,	0–3·2% of Co
0·5-cm. ,,	,,	0–6·4% of Co.

Obtain the percentage of cobalt from a calibration curve prepared under similar conditions.

Calibration

(*a*) *Standard Cobalt Solution*—Dissolve 1 g. of pure oxygen-free cobalt sheet in a minimum quantity of hydrochloric acid. Cover the containing vessel to prevent loss of cobalt by spraying. Cool and dilute to 1 l. with water; 1 ml. of this solution contains 1·0 mg. of cobalt.

(*b*) *Procedure*—Transfer nine 0·5-g. lots of cobalt-free pure iron to 250-ml. conical beakers, and add amounts of standard cobalt solution varied according to the cell being calibrated. Treat these samples as described in method procedure and, using the appropriate cell size, obtain difference readings for the preparation of the calibration graphs.

Notes

(1) Where the alloying quantity of cobalt is between about 6% and 12%, take 0·25-g. sample weight and make up to 0·5 g. with spectrographically pure iron.

(2) Certain types of cobalt alloys may contain refractory carbides; solution of these is best achieved by prolonged digestion before oxidation with nitric acid. Fuming in the reduced condition will also assist decomposition; the solution should then be diluted with water, oxidized, and fumed as in the procedure.

(3) Solutions containing large amounts of silica or graphite should be filtered at this stage. It is only necessary to filter sufficient solution to provide the aliquot portions.

(4*a*) *Reagent Blank*—To minimize the slight absorption due to the nitroso-R-salt when using Ilford 606 filters (about 0·01 drum divisions per cm. of cell size for 30 ml. excess of reagent), the following amounts of reagent are recommended:

0·5-cm. cell	30 ml.
1·0- ,, ,,	20 ml.
2·0- ,, ,,	15 ml.
4·0- ,, ,,	10 ml.

(4*b*) *Nickel Steels*—Some of the nitroso-R-salt added will be consumed by nickel, if present, to the extent of about 0·8 ml. for every 1·0% of nickel in the original sample. The method will tolerate at least 5% of nickel, but quantities in excess of this will require additional reagent.

(4*c*) *Copper Steels*—Similarly, copper consumes nitroso-R-salt. In the absence of nickel, up to 2% can be tolerated, but above this level a further 2·0 ml. of reagent is required for each additional 1% of copper.

IMPORTED ORE HANDLING

Report of a Conference Organized by the British Iron and Steel Federation

In view of previous difficulties with the unloading of ore at U.K. ports, and the need to ensure that facilities will be available to handle more efficiently and quickly the still larger tonnages that will be imported in the future, an Imported Ore Handling Advisory Committee was set up in 1949 to study, on behalf of the iron and steel industry, the problems involved in the transport of ore from overseas ports to the blast-furnaces in this country.

The results of investigations made by BISRA, under the guidance of the Committee, on the design of ore-carrying ships, discharge equipment at ports, and handling and rail-transport facilities, have enabled the Committee to make general recommendations for increasing the efficiency of shipping, discharge, and subsequent land transport of the larger tonnages to be imported.

The British Iron and Steel Federation's Advisory Committee on Development, which has the responsibility of co-ordinating the industry's development plans, is following up the recommendations of the Imported Ore Handling Advisory Committee.

IMPORTED ORE HANDLING CONFERENCE

Under the auspices of the British Iron and Steel Federation, a Conference was held at Ashorne Hill on 16th–17th September, 1953, to discuss recent developments and the best means of further improving shipping and discharge facilities. A series of papers was presented dealing with size of ship; hold design; capacity of discharge equipment in relation to the total tonnage handled; problems of manning in relation to ship design and berth occupancy; recent installations by the Consett Iron Company, Ltd., and John Summers and Sons, Ltd.; type of discharge equipment and trimming machines; and the removal of ore from the dock, its storage, and reception facilities at the works.

The Chairman of the Conference was Mr. **E. T. Judge** (Messrs. Dorman, Long and Co., Ltd.), Chairman of the Imported Ore Handling Advisory Committee and a member of the Advisory Committee on Development.

CHAIRMAN'S OPENING REMARKS

Mr. Judge paid tribute to the ability and effort which had been applied in the past to the study of ore-handling problems. Before the Imported Ore Handling Advisory Committee had been established, special ore carriers were bringing foreign ore to this country, and efficient unloading equipment had been in operation for many years at some ports. Other unloading installations were already under construction, or planned, before the Committee had completed its investigations, and there had also been considerable developments in the land transport of ore.

It was important, however, to consider the problem of imported ore handling as a whole rather than as a series of isolated operations. For example, what might appear to be the correct solution when considering the unloading operation alone might not produce the lowest over-all cost of handling the ore from overseas to the furnace bunkers.

The implementation of the recommendations made by the Imported Ore Handling Advisory Committee rested with the appropriate authorities. The purpose of the Conference was to provide an opportunity for these recommendations to be discussed, in the hope that those responsible would be assisted in taking appropriate and opportune action so that future ore imports might be handled as economically as possible.

SIZE OF SHIP

Dr. **T. P. Colclough,** C.B.E. (Technical Adviser, British Iron and Steel Federation) said that the planned increase in pig-iron production would require a substantial increase in the quantity of ore to be imported. The shipping tonnage available at present, however, was not adequate to transport the additional tonnage of ore. Many of the cargo ships in the ore traffic were small, old, and quite unsuitable in design for rapid unloading. It was recommended that new vessels should be provided specifically for the ore traffic and designed to give the maximum rate of unloading and maximum carrying capacity per foot of draught. These ore carriers should operate on shuttle services, thus permitting the maximum tonnage of ore to be transported at the minimum capital outlay and operating cost.

An important factor limiting the size of a ship was the permissible draught at the ports. The principal foreign and U.K. ore ports could be conveniently classified into three groups, with an available depth of water of 30, 28, and less than 25 ft. These draughts corresponded to ore carriers of 20,000–22,000, 12,000–14,000, and 8000 tons carrying capacity, respectively.

The small carriers could be loaded at any of the supply ports and discharged at practically all the main U.K. ports; the 12,000–14,000-ton carriers could berth at 11 foreign ports and eight U.K. ports; whilst the largest ships would be capable of working between four loading and four British unloading ports, which are or, with relatively minor modifications, could be equipped to handle vessels of this size.

Undoubtedly the use of the largest ship was the most economical, particularly for long voyages, but practical reasons made it imperative to have ships of all three sizes; thus, adequate shipping capacity had to be made available to meet the increasing requirements of the shallow U.K. ports and to bring ore from the overseas shallow ports. There was also an undoubted field of usefulness for the servicing of the deep-water ports by small carriers for relatively short journeys.

The Imported Ore Handling Advisory Committee, therefore, recommended that :

(*a*) The industry should obtain as large a proportion as practicable of large ore carriers (30 ft. draught, up to about 22,000 tons carrying capacity), particularly on the longer deep-port routes

(*b*) A sufficient number of small ore carriers (less than 25 ft. draught, about 8000 tons carrying capacity) should be built to meet the additional requirements of the works served through shallow British ports

(*c*) The remainder of the fleet should consist of medium-size ore carriers (28 ft. draught, about 14,000 tons carrying capacity).

The Executive Committee of the Federation, before the completion of the investigations and on the advice of B.I.S.C. (Ore), Ltd., had already made arrangements for the building of eight 8000-ton and seven 12,000-ton carriers. Two of the smaller ships were in operation.

Discussion : It was suggested that a relatively small expenditure on locks would enable the shallow ports to take a shallow-draught ship of extreme length (comparable, for example, to the American Lake ships) and thus permit the development of a standard type of ship capable of unloading at any British port, with the consequent economies. However, the stresses to which ocean-going ships would be subjected would be very much greater than those in the Lake steamers. Open berths were available on the Great Lakes and ship dimensions were, therefore, not restricted by locks and harbours.

Reference was also made to the recent and current construction of bulk cargo carriers of about 8000 tons carrying capacity, which were well suited to the ore traffic. This appeared to indicate that ship owners favoured the smaller ships. Small ships, admittedly, were more adaptable, and this was an important consideration for general-cargo ships, but the substantial economies effected by the larger carriers could not be denied. This was confirmed by the action taken by Broken Hill Pty. Co., Ltd., in Australia, where the carrying capacity of the ore carriers had been raised from 5500 to 12,500 tons as the length of haul had increased from 1200 to 3000 miles. Carriers of about 50,000 tons capacity were being built for use by the U.S.A.

The economic advantages of the larger ships became more marked as the length of the sea voyage increased. At present such large carriers would have access only to a few British ports, and the question was raised of the suitability of the ore available from distant sources for the works served by the deep ports. It was pointed out, however, that the large carriers need not be restricted to the long runs, since, even on journeys of 1000 miles, they would be more economical than the small carriers, provided that quick turn-round was achieved. The annual savings of the large carriers might be less on short than on long voyages, but they would still be substantial compared with those of the small carriers.

HOLD DESIGN

Mr. **J. S. Terrington** (B.I.S.R.A.) outlined the investigations which had been made to assess the effect on discharge rates of the hold design of general-cargo ships. The records of ore-carrying ships arriving at British ports showed that the unloading rates on the best of the general-cargo ships were about 50% higher than the average, and this was a measure of the minimum benefit to be derived from specially designed carriers.

The study indicated that where possible no obstruction in the hold should be permitted. The hold should be at least 28 ft. across; there should be no 'tween decks; no bottom fillets or hoppering between the side and floor of the hold; no deck overhang; as few transverse bulkheads as possible; no obstructions such as pipes in the hold; and ladders should be installed only where they were essential, and protected against damage by the grab. Where 'tween decks were necessary, in a ship carrying varied cargoes, the height between the 'tween deck and the hold floor should be at least 28 ft., to allow sufficient head-room for the grab to be manœuvred.

The ore carriers should have a minimum number of narrow and centrally placed holds with ballast or flotation tanks on each side and underneath, so that the centre of gravity of the loaded ship would be at a suitable level. The hatch dimensions should as nearly as possible equal those of the hold so that overhanging deck would be reduced to a minimum, and the designers of ships and of unloading equipment should co-operate to match the arrangement and dimensions of the ship's hatches with the requirements of the unloading equipment.

These measures would enable the discharge grab to work centrally over the hold, would ensure that the unloaders had sufficient outreach from the wharf to reach the far side of the hold. Such holds should not

require trimming, although their design would facilitate the use of mechanical trimmers where necessary. The digger grab should be able to remove almost all the ore, thus practically eliminating the time-consuming and expensive trimming. It should be possible to increase the unloading rate by at least 30% over that of general-cargo ships of similar capacity. This would reduce the unloading costs per ton of ore and also allow the carrier to make more journeys each year.

Discussion : There was general agreement with the principles elaborated, and reference was made to the importance of correct hold design in minimizing damage to the ship by the grabs during discharge. Mention was made of the possibility of altering the holds of general-cargo ships to exclude ore from the wings of the ship, thus improving the rate of unloading. Hoppering of the holds of Liberty ships had enabled the average rate of discharge to be raised from 100 to 500 tons per hour. Mr. Terrington did not consider that the conversion of general-cargo ships was necessarily a good solution, as hoppering at a suitable angle would take up useful space in the hold.

CAPACITY OF DISCHARGE EQUIPMENT IN RELATION TO THE TOTAL TONNAGE HANDLED

Mr. **R. T. Eddison** (B.I.S.R.A.): The total cost of discharge of a ship comprises the cost of operating the unloading equipment itself and, not always taken into account, the cost of the ship's time in port. Investigation had shown that there was very little difference in the cost of operating different types of unloading installation, provided that they were being operated at the same berth occupancy (*i.e.*, the proportion of the total possible time that the berth is occupied by a ship). To obtain quicker turn-round and reduced total discharge cost it was necessary to achieve much higher discharge rates and lower values of berth occupancy than at present.

It was recommended that for maximum efficiency all British ports should be equipped to have an unloading capacity high in comparison with the tonnage that would actually be handled. This would secure the lowest total cost of discharge, although the berths and their equipment might, on an average, be unoccupied for between one-third and two-thirds of the time according to circumstances. Equipment at the major ports should be manned continuously whenever a ship was in port.

At each port the required capacity should be obtained with faster equipment on as few berths as possible. With present methods of trimming, existing general-cargo ships could be discharged at an average rate of about 6000 tons per day with suitable equipment worked continuously. A port should not have a second berth until more than 1½ million tons per year had to be handled, or a third berth until the tonnage exceeded 3–3½ millions. Efforts should be made to avoid having ports handling small quantities, as rates of discharge high enough for rapid turn-round could not be justified economically with imports below about ¾ million tons a year.

Discussion: The importance of having dock storage or land transport facilities to keep pace with the peak rates of unloading was stressed.

It was suggested that additional berths should be used to deal with the less suitable ships, thus enabling the high-capacity installation to be worked to its utmost advantage. Mr. Eddison's view was that such an arrangement could only be economic in certain exceptional circumstances. The provision of a new berth would increase capacity and, without a commensurate increase in the tonnage to be handled, would increase costs.

A problem that faced some of the ports unloading relatively small tonnages of ore (and particularly those which could take large ships) was that the annual imports were not sufficient to justify the installation of equipment which would give suitably high rates of discharge. However, the first need was to ensure that the large-intake ports were being developed on the right lines; then the possibility could be considered of increasing the tonnages handled by some of the smaller ports, *e.g.*, by concentration.

The extent to which quicker turn-round would be reflected in reduced charter rates was questioned. It was suggested that tramp rates were in the main influenced by world trading conditions rather than by turn-round times. Others expressed the view that, except in times of extreme shipping shortage, quick turn-round was bound to influence charter rates. Average rates to Rotterdam quoted on the open market were several shillings a ton cheaper than the rates to any British port, mainly because of the quicker turn-round time and lower unloading charges at Rotterdam. Whatever might be the position regarding voyage-charter rates, a very substantial benefit would accrue from quicker turn-round in the case of time-chartered ships.

PROBLEMS OF MANNING IN RELATION TO SHIP DESIGN AND BERTH OCCUPANCY

Mr. **W. F. Cartwright** (Steel Company of Wales, Ltd.) referred to the practice at Port Talbot, where three shifts were worked, including all holidays and week-ends.

The most effective means of speeding turn-round, short of supplying new equipment, was to increase the number of working shifts per year and to make the fullest effective use of the working time available in each shift. At Rotterdam, for example, labour was available for continuous working and, in addition, labour agreements allowed for transfer from one ship to another during the shift. The importance of continuous working arrangements in speeding ship turn-round could not be over-emphasized.

Mr. Cartwright referred to the arrangements whereby dock labour was made available under the National Dock Labour Scheme, and suggested that the method of employment of dockers in iron-ore ships was not conducive to the maximum manpower efficiency. For example, the experience of the dockers varied and, with modern high-capacity discharging equipment, casual labour slowed up the work considerably. Further inefficiency arose because the precise time when a large number of dockers would be required in the hold was not known. Efficiency might be improved if the wharf operator employed a regular gang who would man the ships according to actual requirements. The success of such a scheme would obviously depend on the arrival of ships with reasonable regularity. Further difficulties would arise if there were large variations in the type of ship.

Mr. Cartwright also stressed the importance of communications, not only between the ship and port but also between the wharf-side, ore stockyard, and marshalling yards. Wireless communication with ships at sea would enable most of the maintenance of the discharge equipment to be undertaken during periods when berths were idle, thus reducing maintenance-stoppage costs. Improved internal communications would ensure that the operators, including crane drivers, transfer-car drivers, and railway-locomotive shunters, always knew in advance what they had to do, and this should effect considerable savings.

Discussion: The importance of the co-operation of labour in the successful application of the recommendations was emphasized.

The experience, both as ship owners and ship charterers, of one large firm handling bulk materials was that continuous manning was the only way of running ship discharge plant efficiently. The key point was to train one's own trimming labour and crane drivers, whilst adequate plant maintenance was also of major importance. Another company engaged on bulk discharge was operating a system of inter-communication which had proved very successful. In addition, labour agreements had been negotiated permitting transfers from ship to ship and, with the introduction of mechanical trimmers, requiring only the minimum number of men to clean out inaccessible places.

DESCRIPTION OF RECENT INSTALLATIONS

Mr. **F. B. George** outlined the ore-handling scheme installed by the Consett Iron Company, Ltd., in conjunction with the Tyne Commission and British Railways. The river terminal consisted of a quay dredged to 35 ft. at low water and capable of taking ships of up to 25,000 tons capacity at all states of the tide. The quay was equipped with five 10-ton Kangaroo-type cranes, each with a capacity of 300 tons per hour. A belt system delivered the ore to ten storage bunkers each of 1000 tons capacity. Two scale cars discharged the weighed ore into ore pockets. A complete train of eight or nine 56-ton capacity side-discharged bogie wagons was positioned under the ore pockets and loaded in a matter of seconds by the simultaneous release of air-operated doors. On arrival at the works after a 15-mile journey, the train, with a load of approximately 500 tons of ore, was run on to the terminal ore-receiving bunkers. There the ore was discharged into the bunkers in about fifteen seconds through the air-operated doors. The empty train then proceeded immediately on the return journey. The installation was easily capable of discharging and handling over 10,000 tons of ore per 24 hours. The yearly delivery was expected to be over $1\frac{1}{4}$ million tons.

Mr. **J. F. R. Jones** described the scheme adopted by John Summers and Sons, Ltd. The Mersey Docks and Harbour Board had made available at Bidston Dock two adjacent berths with a 28 ft. draught, which were at all times capable of taking ships of about 14,000 tons carrying capacity. The $12\frac{1}{2}$-ton unloaders which were being installed were capable of discharging about 360 tons per hour each, although the normal rate was not expected to exceed about 200 tons per hour. The unloaders spanned four railway tracks and had two hoppers, each of which could be moved over two tracks. The ore, dumped into the hoppers from the grab, would be fed into double-bogie hopper-bottomed wagons of about 46 tons carrying capacity (this could be increased to about 60 tons with the permitted increase in axle load). Trains of 1000 tons gross (equivalent to about 750 tons of ore) would be hauled by British Railways to the works at Shotton. There the train would be divided into two parts and each put separately by works' locomotives on to a line of 42 25-ton capacity hoppers. The whole train could be turned round at the works in about an hour. A tippler had been placed at the end of the line of bunkers to deal with very sticky ores. The scheme when completed would be capable of handling about $1\frac{1}{2}$ million tons a year.

Discussion: Mr. **Towndrow** (Colvilles, Ltd.) outlined some of the essential principles in the planning of the proposed ore-handling scheme on the Clyde. Each unit of the discharge and handling system should be permitted to work at the most appropriate rate with suitable intermediate buffer storage capacity, as the matching of the speed of the different units involved extremely heavy capital expenditure. Consideration was being given to the installation at each berth of two unloaders with a combined capacity of about 1000 tons per hour. To avoid the dangers inherent in handling ore into very large storage bunkers, some form of buffer stocking and reclaiming facilities would be provided at the dockside, and at the works the ore trains would be discharged into a grabbing trough at the stockyard. Trains of approximately 900 tons gross would be turned round at the works in about one hour.

The remainder of the discussion centred around the possible difficulties associated with bunker-storage schemes, and the relative merits of the large-capacity bogie wagon and the general-purpose 27-ton wagon.

TYPES OF DISCHARGE EQUIPMENT AND TRIMMING MACHINES

Dr. **H. R. Mills** (B.I.S.R.A.) stated that to achieve average discharge rates of at least 6000 tons a day with two-shift working it was necessary to have the biggest and most expensive equipment, but with continuous working there was a range of equipment available which could give average unloading rates of 5000–8000 tons a day.

Slewing and luffing cranes of approximately 10 tons capacity were satisfactory for tonnages up to about $\frac{3}{4}$ million tons a year, provided they were worked continuously. The speed of operation of this type of crane decreased with increase in size because of the jib inertia. Kangaroo-type cranes had a luffing action only and were, therefore, faster in action for the same size. Four 10-ton Kangaroo cranes worked continuously would handle $1\frac{1}{4}$–$1\frac{1}{2}$ million tons a year, and two man-trolley unloaders of about 20 tons capacity would give the same rate of unloading. More than two unloaders could not be usefully employed on one berth, however, because of their length over the buffers. Larger machines than those used at present, particularly larger Kangaroo cranes, were worth considering for tonnages of $1\frac{1}{2}$–2 million tons a year, to avoid the need for a second berth. Other types of discharge equipment included the rope-trolley or tower-crane unloader and the Hulett unloader, but recent American practice appeared to favour man-trolley unloaders.

The trimming period was much longer than it needed to be, because of the British practice (unlike that in Antwerp, for example) of separate grabbing and trimming periods. Another possibility of speeding up trimming was to use mechanical aids. Several ports had made trials with mechanical shovels, bulldozers, and overhead bucket-loaders for trimming, but Dr. Mills felt that none of the machines at present available was really suitable. A machine was required that was light, small, and robust. He recommended that trials should be made with bulldozers with pulling blades, and with winch-driven scrapers or slushers.

Discussion: Dr. Mills had compared Kangaroo cranes and normal slewing cranes working without hoppers. There was no reason, however, why the normal slewing crane should not work to a separate hopper at the quayside; capacity could be increased considerably. An installation of this type for bulk sugar discharge was described. Mention was also made of an American man-trolley unloader which discharged into a hopper between the legs of the unloader. The ore was then fed from the hopper to the ore trough by belt conveyor. This speeded up discharge considerably, as the man-trolley travelled no more than about half the normal cross-travel back to the ore trough.

A trimming machine was referred to, which had all the characteristics of a crawler tractor but was mounted on pneumatic tyres, and which could operate without damage to the hold. It was suggested that the demand in this country and abroad would not be large enough for

a machine specifically designed for the trimming of iron ore. The demand in future would be expected to be even less, as it was aimed to provide ships which did not require any trimming. Dr. Mills emphasized, however, that imports of iron ore were to increase substantially within the next five years and any new ships that might be built would at the most only carry the increase in tonnage. In five years' time there would be at least as much ore as at present to be discharged from general-cargo ships, so that the necessity for mechanical aids in trimming would not decrease.

LAND TRANSPORT AND STORAGE FACILITIES

Mr. **M. D. J. Brisby** (B.I.S.R.A.) emphasized that unless it was possible for rail transport services to match peak unloading rates (and in general this would only be possible below about half a million tons a year) buffer storage accommodation in the form of sidings, stockyards, or bunkers should be provided as near as possible to the point of ship discharge. This would ensure that all subsequent services need only operate at the works' intake rate, and the cost of these extra facilities would be small compared with the value of quick discharge. Works' discharge systems should provide adequate storage and unloading equipment, so that trains arriving at irregular intervals could be unloaded without causing congestion.

A major traffic operating problem in congested areas was the limitation of line capacity, and serious consideration should be given by British Railways to the running of heavier trains (up to 1000 tons of ore) on the important routes, as this would enable greater tonnages to be carried at reduced cost without increasing line occupation.

The 27-ton iron-ore tippler wagon was at present the most suitable wagon for use on tipplers, and the best two-axle hopper wagon was the 24-ton iron-ore wagon; British Railways were developing a new 25½-ton hopper wagon. Iron ore was still frequently carried in other types of wagon, most of which were unsuitable for the purpose, and the immediate policy should be to build enough of the 27-ton tippler and 24-ton (or the projected 25½-ton) hopper wagons to eliminate all other wagons from the ore traffic. This would mean that a number of works would have to improve their discharge facilities to take the heavier wagons.

The present load restriction of 17½ tons per axle for iron ore traffic, was lower than in most countries and the policy should be to raise the axle load to 22½ tons, at least over the major iron-ore routes.

The suitability of bogie wagons for use in the United Kingdom remained controversial, but the Imported Ore Handling Advisory Committee had recommended that bogie wagons merited consideration only when they were of the largest possible size (at least 60 tons capacity) and when they could be used in heavy trains, fitted with automatic brakes, for a fast shuttle service.

Discussion: Tribute was paid to the helpful collaboration of the Railway Executive in dealing with the transport problems of the industry.

Regarding the conditions under which a special rail-transport scheme became an economic proposition, Mr. Brisby said that the main point was not the tonnage handled, but the kind of line over which the traffic had to pass ; special schemes were necessary for very congested areas.

Representatives of the Railway Executive pointed out that to discard the less suitable ore wagons while they were still in working condition was difficult, particularly when steel was in short supply. Regarding the problem of axle loading, there were about 37,000 bridges on British Railways routes, many of them unable to take axle loads of 22½ tons. A detailed investigation covering all iron-ore routes was in progress, however. With wagons designed to take a 22½-ton axle load there would clearly be less flexibility in wagon distribution. Train loads and weights of trains were dependent on many factors, including the gradients of the routes and the safe limits for length of train and stopping distance. Special signalling arrangements would be essential for very heavy trains. Investigation had shown that the cost of repairs and renewals per ton of capacity was much higher on the bogie than on the two-axle wagon.

HISTORICAL NOTE NO. 34

The Blacksmith in 17th Century England

By H. R. Schubert

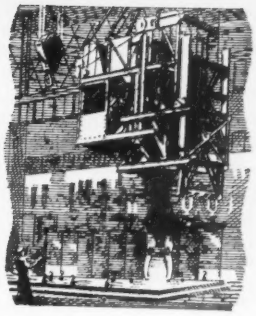
JOHN EVELYN (1620–1706) is well known as an author by his "Sylva", a book published in 1664 which deals with trees and timber. The diary he kept throughout his career is of equal value, as it reflects the author's wide interests. In 1654 he stayed at Broad Hinton with a relative who showed him a lock for a door which, as Evelyn worded it, "for its filing and rare contrivances was a master-piece yet made by a country-blacksmith". This remarkable piece of work induced the author to praise in his diary the excellent work achieved by the English blacksmiths of his day. He wrote as follows : "But, we have seen watches made by another with as much curiosity as the best of that profession can brag of ; and, not many years after, there was nothing more frequent than all sorts of ironwork more exquisitely wrought and polished than in any part of Europe, so as a door-lock of a tolerable price was esteemed a curiosity even among foreign princes".[1]

Manuscript received 11th September, 1953. Dr. Schubert is Historical Investigator to The Iron and Steel Institute.

[1] Diary and Correspondence of John Evelyn, F.R.S., edited by Wm. Bray, vol. I, p. 293, London, 1850.

IRON AND STEELWORKS ENGINEERING

THE IRON AND STEEL ENGINEERS GROUP



Steelworks Waste-Heat Boiler Practice

By R. McDonald

SYNOPSIS

The aim of this paper is to define and illustrate the application and efficient operation of waste-heat boilers in the steel industry. The paper discusses the historical background, design and layout of plants, and operational conditions based on practical experience. Investigations into the further extraction of heat after the waste gases leave the boiler are also discussed, and the paper concludes with some operational details derived from an economizer recently installed to operate in series with a waste-heat boiler. 850

THE means whereby the waste heat leaving industrial furnaces in the flue gases may be recovered and made to perform useful work has been the subject of intensive study for almost a century. In the metallurgical industry the most widely used method of waste-heat recovery is to pre-heat fuel gas and combustion air by means of regenerators or recuperators, thereafter discharging the gases through a boiler and using the maximum proportion of the remaining sensible heat to generate steam.

HISTORICAL

The earliest applications of boilers for the recovery of the sensible heat from furnace exhaust gases were made to the puddling and mill furnaces of the wrought-iron industry in the early 1860's. These early types of boiler, simple in design, were thermally inefficient but, operating with inlet gas temperatures of 1200° C. and over, were capable of supplying the steam requirements of the works.

With the introduction of the steelmaking processes more power was required to drive the rolling mills and, puddling furnaces being no longer required, the additional supply of steam had to be generated by independently fired boilers. In the case of open-hearth furnaces the application of regenerative principles to the pre-heating of combustion air and fuel gas resulted in waste gases substantially lower in temperature being available for steam production.

In March, 1911, at a meeting in Glasgow, T. B. Mackenzie[1] presented the first theoretical thesis on waste-heat utilization. He outlined the hypothetical case of a 50-ton open-hearth melting furnace with a production rate of 3·37 tons of ingots per hour and a fuel consumption of 9 cwt. of coal per hour. From a calculated thermal balance he showed that, by introducing 42,000 cu. ft. of producer gas to augment the heat units contained in the waste gases, enough steam could be raised to meet his estimated rolling requirements. With this method of generating steam he calculated that the fuel saving would be almost 42%. He advocated that a boiler should be placed between the furnace and the chimney, as had been previously done with puddling and reheating furnaces, and, owing to the lowering temperature of the waste gases, using an induced-draught fan to maintain draughting conditions in the main unit.

As a direct outcome of this paper an experimental Babcock and Wilcox water-tube boiler, fitted with Green's economizer and Keith Blackman induced-draught fan, was installed on a 30-ton melting furnace at Dalzell works in the same year. The results amply justified Mackenzie's views, as with a production rate of 2·25 ingot tons/hr., the amount of steam generated was 1244·5 lb. ' from and at ' per ton of ingots, which, when compared with fuel boilers generating at 7 lb. of steam per lb. of fuel, represented an equivalent fuel saving of 177·8 lb. per ton of ingots produced.

Following this successful experiment, waste-heat boilers with economizers and fans were applied to all the furnaces at Dalzell works, and subsequently in the other works in the group. Results of various tests taken on some of these installations are recorded in a paper presented by Mackenzie[2] in 1918. By 1924 Colvilles had 25 waste-heat boilers in service and at least six other steel-producing firms in Great Britain had adopted waste-heat boilers of various types. In America, waste-heat boilers were also being extensively installed, and, in a further paper,[3] Mackenzie quoted performance results which confirmed those obtained in the installations already referred to.

Manuscript received 27th October, 1953.
Mr. McDonald is with Colvilles, Ltd.

In 1921 a new design of fire-tube boiler for the recovery of waste heat was introduced for Spencer-Bonecourt by P. St. G. Kirke. This boiler was designed on the principle of using high gas velocities to obtain high rates of heat transmission. These conditions were obtained with a high tube length/diameter ratio. They were self-contained units, and thus were not affected by air infiltration, a defect which developed under high suction conditions with water-tube boilers, whose brick settings developed cracks as a result of expansion and contraction due to the varying inlet gas temperature during week-end and other shutdown periods. The long tube length was a disadvantage where site conditions were restricted, owing to the space required for tube cleaning and tube withdrawal.

In 1933 Kirke evolved a fire-tube with a sinuous form, and this has proved a most important development in waste-heat boiler design in recent years. Kirke claimed that by the development of turbulence in gas flow along the full length of the tube at moderate velocities, the heat transmission would be accelerated by as much as 150%. For equal heat-transfer efficiency the sinuous-flow tube has a greater diameter and shorter length than a straight tube, factors which reduce the time required for tube cleaning and the floor space required for the boiler installation. Since its introduction in 1921 the fire-tube waste-heat boiler has gradually superseded the water-tube boiler, and new installations have been almost exclusively of this type.

One notable exception was the installation in 1947 of eight controlled-circulation water-tube boilers by the Steel Company of Wales Ltd., in conjunction with their new 200-ton open-hearth furnaces.[4] Operating with 350 lb./sq. in. and a steam temperature of 399° C., these boilers are capable of producing under average gas-temperature conditions about 12,500 lb. of steam per hour.

Colvilles Ltd. first introduced the Cochran Sinuflo type of waste-heat boiler in 1937, when two units were installed at their Glengarnock works, and for subsequent replacements and new installations have used exclusively this type of boiler on their open-hearth furnaces and soaking pits. There are now 34 such boilers in service throughout the various works

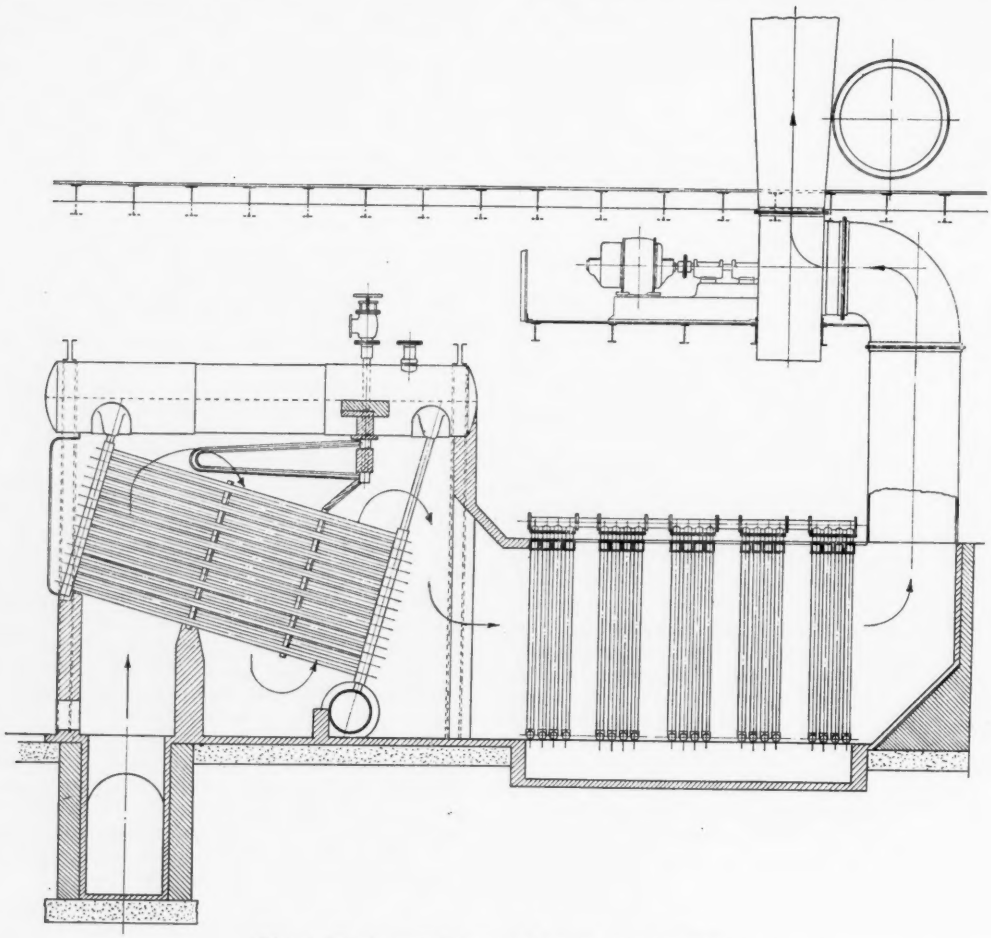


Fig. 1—Early waste-heat boiler (Dalzell works)

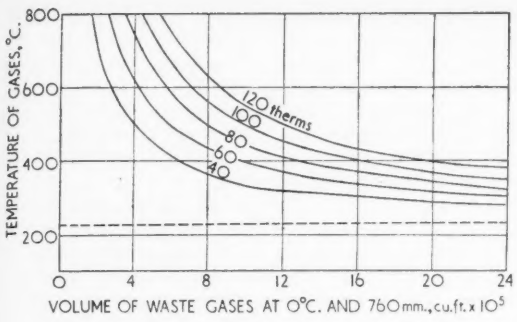


Fig. 2—' Recoverable ' heat above 230° C.

of the group. Figure 1 shows an early type of waste-heat boiler installed at Dalzell works.

FACTORS INFLUENCING INSTALLATION OF WASTE-HEAT BOILERS

In considering the installation of waste-heat boilers at any specific plant, an assessment must first be made of the quantity and grade of heat which may be available for recovery. This quantity is taken as the sensible heat in the gases above the permissible exhaust temperature which, in practice, is seldom less than 38° C. above the saturation temperature at the operational pressure. Figure 2 shows ' recoverable ' heat above 230° C. Secondly, it is necessary to estimate the initial capital and expected operating costs of the plant required for this heat extraction.

The initial temperature and volume of the gases will determine the type and size of the boiler required. In the case of open-hearth and soaking-pit furnaces, average waste-gas temperatures range from 500° to 650° C. Higher temperatures of, say, 900° C. and over require special consideration for efficient operation, and for temperatures of 400° C. and under the size of the boiler would be out of all proportion to the quantity of steam produced.

An assessment of the economic possibilities of any waste-heat installation in terms of steam generated will involve a close study of all matters connected with steam raising and utilization within the works. If all process units are supplied from a general steam ring-main interconnected with fuel-fired boilers, and if the steam from the waste-heat installation under consideration is fed into this common line, there will be an equivalent reduction in steam produced from the fuel boilers, with a consequent saving in fuel. As steam generation from waste gases can only be effected when the furnaces are operating, sufficient fuel-fired boiler capacity must be available to maintain the supply when any main production unit goes off for repairs. In addition, unless there is auxiliary firing on the waste-heat boilers, steam must also be provided from fuel-fired boilers for starting up the various process units after shutdown periods. In any industrial furnace, however, maximum efficiency in the utilization of heat input within the furnace itself must be the first essential, and steam generated by waste heat should be considered as a by-product only.

DESIGN

General

The exhaust gases from open-hearth furnaces are large in volume but low in temperature, and heat transfer is effected mainly by convection. The effectiveness of heat transfer or extraction efficiency in waste-heat boilers is primarily a question of design. Water-tube boilers, normally designed for radiant-heat transfer, when applied as waste-heat boiler units have the tube banks suitably arranged with the necessary baffles to give a long gas path and changing direction in gas flow, ensuring effective heat recovery by convection.

Fire-tube boilers are designed on turbulent-flow characteristics and rely for their effective heat transfer on the scrubbing action of the gases along the heating surface of the tubes.

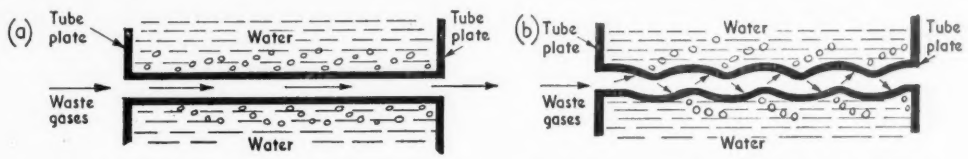
Favourable conditions are created by high gas velocities superseding streamline flow by turbulent flow, or by mechanical methods of breaking up the flow stream. The former is the method used for the Spencer-Bonecourt–Kirke boiler, and the latter for the Cochran Sinuflo boiler. Figure 3 shows straight tube and Sinuflo tube characteristics.

Limit of Heat Extraction

The exit temperature of the gases leaving the boiler should be above the saturation temperature at the boiler pressure, thus ensuring continuous heat transfer from the gases to the water. In practice the gas temperature varies between 55° and 77° C. higher than the saturation temperature.

Advantages and Disadvantages of the Two Basic Designs

Water Tube (Natural Circulation and Forced Circulation)—The advantages of water-tube boilers are their capacity for handling large quantities of high temperature gases and for generating steam at high pressures; in the earlier designs, the water side of the tubes could be cleaned by a rotary cutter wheel in the event of scale deposition.



Gases passing straight through the tube. Hot gases merely rub against the side of the tube, gases in the centre never touch the sides.

Gas impinging against the sides of the tube. Large bubbles at inlet end, where gases are hottest, decreasing as heat is extracted. Small bubbles due to gases rubbing against the sides are not shown.

Fig. 3—Straight-tube and Sinuflo-tube characteristics

The main disadvantages are air infiltration through the brickwork setting, whether open or steel-encased, owing to high suction conditions in the boiler, and the difficulty of keeping the gas side of tubes clean. In open-hearth practice adhesive deposits are experienced which cannot be effectively removed by normal blower arrangements, and heavy dust deposition occurs, which can become so serious that draughting conditions are affected, thereby reducing furnace productivity. Loss in heat transfer through the tubes increases the exhaust gas temperature, with consequent loss in steam generated. Under these conditions the boiler must be by-passed and opened up for manual cleaning.

Fire Tube—The main advantages are the fact that no brickwork setting is required, thereby avoiding losses by air infiltration and reducing radiation losses to a minimum; compactness in design (specially suitable where space conditions are limited); ease of maintenance of the gas side of boiler tubes and superheaters; and the fact that, where the boiler is a twin unit and is in operation continuously between holiday periods, the boiler can be cleaned, prepared for inspection, and ready for service again in three days, if necessary.

Disadvantages are that only partial manual cleaning of the water side of boiler tubes is possible, owing to the close nesting of tubes, and strict attention must be given to feed-water conditions, and that air infiltration at the access doors for tube cleaning increases the fan power necessary for exhaust discharge. On an average there is 1% drop in CO_2 between boiler-tube outlet and induced-draught fan inlet, equal to 16% increase in excess air with drop from 10% to 9% of CO_2 (fuel oil) and increase in gas weight by about 10%. This does not affect heat-extraction efficiency in the boiler.

All subsequent notes in this paper refer to fire-tube boilers in operation with open-hearth furnaces.

Induced-Draught Fan Design

Furnace availability can only be increased by additional draught, and waste-heat boiler installations are normally designed with induced-draught fan capacity to provide this increase in draught where there is danger of chokage within the regenerators.

In view of the importance of maintaining the required draughting conditions in steel production during a whole campaign period of possibly 26 weeks, and where gas temperatures at the fan inlet vary from 230° to 270° C. with a continuously changing CO_2 percentage together with gradually increasing resistance in the system, the fan performance should be designed on the maximum conditions of temperature and resistance and minimum CO_2.

LAYOUT

General

Continuous furnace operation must be the first consideration in the layout of any waste-heat boiler plant. To obtain maximum gas-temperature conditions at the boiler inlet, the boiler plant should be installed as near to the furnace reversing valves as site conditions permit, and the exhaust-gas flue system from the checker outlet to the boiler inlet should be designed to ensure minimum air infiltration and heat

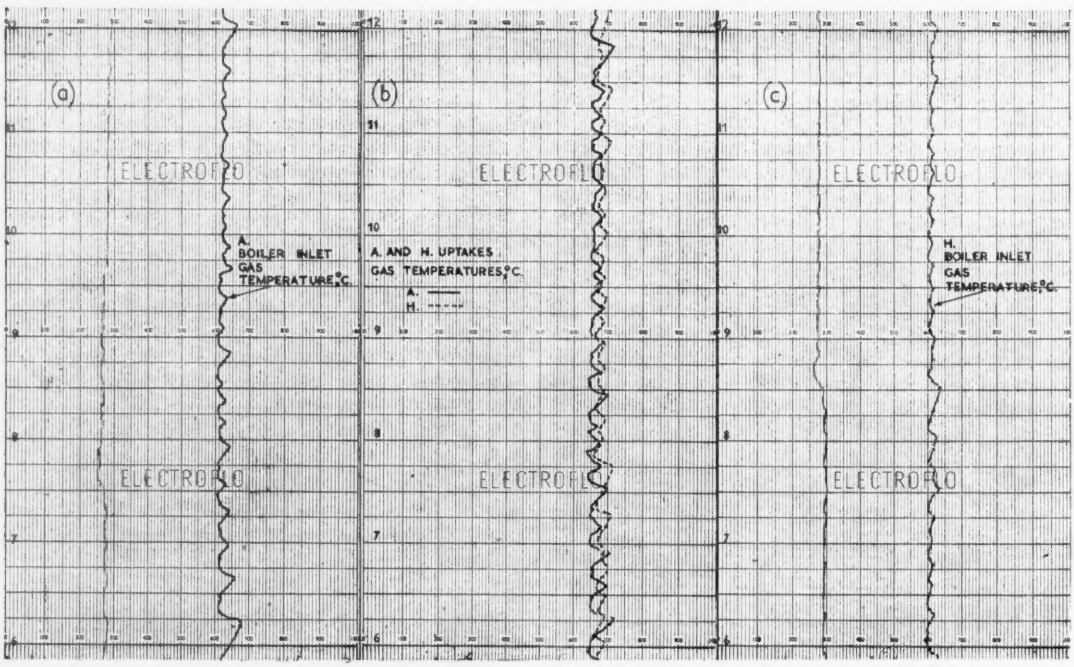


Fig. 4—Recording of exhaust gas temperatures (uptakes and boiler inlets)

loss by radiation. Exhaust flues should be built with a minimum number of bends to minimize draught loss between the checkers and the inlet to the boiler.

The damper-type reversing valve and steel flues, adequately lined with efficient insulation slabs protected by suitable firebrick on the gas side, reduce air infiltration and heat loss by radiation to a minimum. The increase in efficiency obtained by lining the steel tube with top-grade insulation material is illustrated in Fig. 4, which shows recordings of the temperatures of the exhaust gases from two furnaces, the gases passing to a twin boiler through two steel flues lined with different grades. Figure 4*b* shows the gas temperature in each tube at the uptake in the valve pit, and Figs. 4*a* and *c* show the gas temperature in each tube at the boiler inlet. Furnace tube *A* is lined with the higher-grade insulation, and the difference in temperature drop averages about 35° C. more in tube *H*, which is lined with the lower-grade material.

In fire-tube boilers at floor level, sufficient space must be provided longitudinally to allow for tube withdrawal and cleaning. Induced-draught fans on fire-tube boilers are in some installations fitted on the boiler-floor level with the stack to the inside; it would be advantageous to install them above the boiler, if

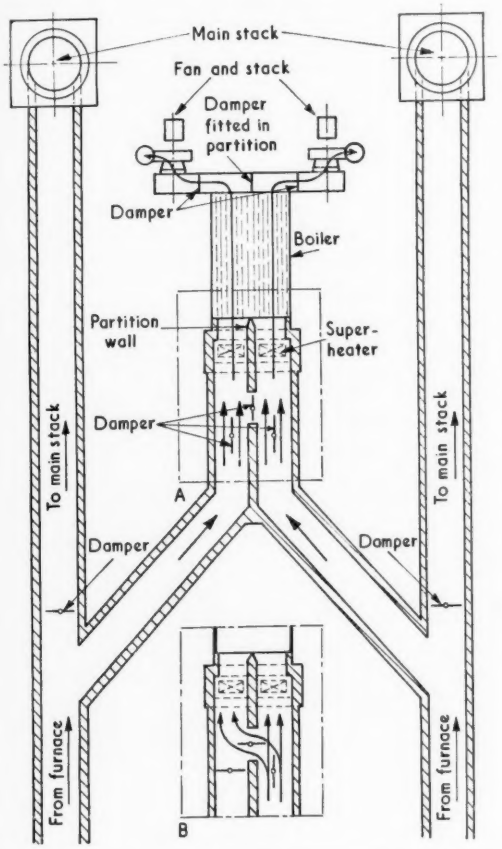


Fig. 5—Damper arrangement of twin boiler: *A* = 2 furnaces, *B* = 1 furnace operating on boiler

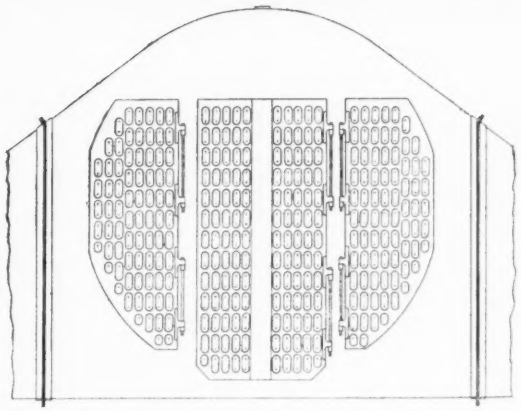


Fig. 6—Cleaning holes in outlet casing

only to reduce radiant heat where the operator has to walk while cleaning the tubes.

Exhaust to Main Chimney

The exhaust chimney from a waste-heat boiler should be connected to the main chimney. This arrangement has a twofold advantage:

(i) The main chimney is always hot and the waste gases can be by-passed immediately, in the event of failure in the boiler

(ii) Fan power required is reduced, owing to the additional draught conditions created by the height of the main chimney, thus reducing electrical supply costs.

Damper Arrangement

The damper arrangement at the boiler inlet should be such that if any breakdown occurs in the boiler the waste-gas flow can be immediately by-passed to the main chimney.

In twin-boiler installations, each of the two furnace waste-gas flues should have a separate by-passing arrangement, so that when either of the furnaces is off for repairs only the gases from the operating furnace are passing through the boiler. A damper arrangement must also be provided at the boiler inlet so that when one furnace is in operation the exhaust gases pass through all the boiler tubes. To prevent distortion along the bottom edge at high inlet temperatures, dampers should be totally withdrawn from the flues when not required. Figure 5 shows the damper arrangement for a twin boiler.

Hinged doors without fixings must be provided on the casing of the inlet products chamber in case of explosions due to the presence of combustible gas in the flue. The faces of the doors and frames should be accurately machined to prevent air infiltration when closed.

Feed-Water Supply

Increased furnace availability is obtained when operating a waste-heat boiler in series with the furnace; the boiler should therefore never be by-passed unless there is an actual failure in the boiler itself.

All feed-water lines, suction and delivery, should be in duplicate. The two discharge lines should be

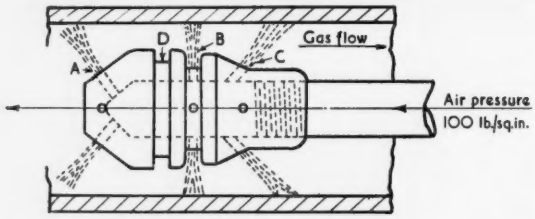


Fig. 7—Air-lance nozzle

interconnected with a suitable valve arrangement, so that each check valve on the boiler can be operated from either line. Provision should also be made for emergency supply to the feed tank if the normal supply fails. In any new installation the approximate feed-water temperature to the feed-pump suction should be calculated, as this determines the head necessary for efficient pump operation. If a flow-recording unit is designed and installed to operate at pump level and, owing to increase in the feed-water temperature at the pump section, it becomes necessary to raise the unit to give the required head, thus reducing the head between the feed tank and the recording unit, the maximum water flow through the float valve will be proportionately less. Where, because of the head conditions between the main water-supply unit and the feed tank, the recording unit must be installed between the feed tank and the pump suction, the design of the float valve is of vital importance, owing to the small reserve of water in the recording-unit tank. In a recording unit of a standard design and 100,000 lb./hr. capacity, the reserve is about 850 lb. To ensure ample supply to the feed pump suction, should there be a sudden demand due to low water conditions in the boilers, the maximum flow available through the float valve should be at least 50% above the normal flow.

Normally, where head conditions are suitable and the unit is of the type fitted before the pump, the water flow is from the recorder to the feed tank, and the pump takes its supply from the feed tank.

Flow recorders fitted on the discharge side of the pump give accurate readings with rotary pumps, but give erratic readings with ram pumps, owing to the fluctuation at the end of each stroke.

De-aeration

A unit for removing oxygen from the feed water before it enters the feed lines should be considered as part of any waste-heat boiler plant installation. Without this unit, feed lines become partial de-aerators and renewals are frequent. This appears to be more evident at about 60–71° C. A typical analysis of the deposit from a piece of corroded feed pipe shows 88·8% of iron oxide.

OPERATIONAL CONDITIONS

Boiler-Tube Cleaning (Gas Side)

A large amount of dust is borne by the waste gases from industrial furnaces, the quantity deposited within the tubes depending on the nature of the materials charged to the furnace and velocity conditions through the furnace system. Heavy dust deposition in the tubes can seriously retard heat transfer, resulting in higher exhaust-gas temperature, with consequent loss in steam production, and the increased resistance through the tubes necessitates additional fan power to maintain draughting conditions in the furnace system. The need for keeping the heating surfaces clean is therefore very important. Holes are provided in the outlet casing opposite each tube for cleaning purposes (*see* Fig. 6).

Various methods have been used for tube cleaning, but in the author's experience the only efficient method is to pass a suitable nozzle right through the tubes, using dry clean air at a pressure of not less than 100 lb./sq. in. The tubes need to be wire-brushed occasionally to remove adhesive deposits. A proprietary air lance can normally make a good job of cleaning the tubes but, as it must be operated from the outlet end of the boiler against the gas flow and suction conditions, the dust from each individual tube passes back through other tubes and there is a gradual build-up 5–6 in. from the inlet end which can only be removed by wire-brushing.

The author has designed and experimented with various types of nozzle, and Fig. 7 shows the most successful. Air at a pressure of 100 lb./sq. in. blows through holes *A*, *B*, and *C*. Air through *A* cleans the outlet tube plate, that through *B* cuts the deposits from the tubes, and that through *C* cleans a portion of the inlet-tube plate each time the nozzle projects through the tube, and also discharges the dust into the outlet chamber when the nozzle is being withdrawn. The dust in suspension is discharged through the fan to the atmosphere. Groove *D* carries a ring, easily renewed, which prevents wear on the nozzle and also acts as a scraper when passing the nozzle through the tubes.

Boilers connected with open-hearth furnaces must be thoroughly cleaned every 24 hr. It is usual practice to clean one-third of each boiler per shift, which ensures a continuously clean portion on each boiler.

Superheater Tubes (Gas Side)

Normal facilities provided are not sufficient to maintain these tubes in a continuously clean condition. Where furnaces are damped down at the end of each week the tubes can be given a partial clean through the side doors, but the steam temperature

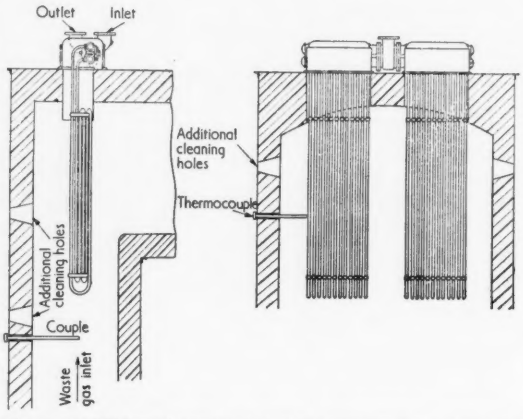


Fig. 8—Additional access holes for cleaning superheater tubes

shows a gradual fall throughout the week, and where the steam is used for power generation the temperature must be maintained as high and as steady as possible.

Where furnaces are in continuous operation seven days per week, facilities must be provided to clean all parts of the tubes at least once per shift. With similar conditions at inlet products chamber (*i.e.*, gas temperature and gas weight) clean tubes show a rise of 16·6–19·4° C. in steam temperature compared with dirty tubes. Figure 8 shows additional access holes provided by the author for efficient cleaning. Figure 9 shows the recorded steam temperature from a twin boiler when the tubes are kept clean.

Induced-Draught Fans

At inspection periods induced-draught fan impeller blades must be cleaned thoroughly. Any build-up of hard deposit affects the impeller balance, which can cause excessive wear on the bearings. On twin boilers as at present designed, cleaning is only possible at holiday periods, unless the boiler is by-passed from both furnaces, a condition which would affect the general steam supply.

Boiler-Tube Cleaning (Water Side)

This is undoubtedly one of the most serious problems in a waste-heat boiler of fire-tube design. The shell diameter is restricted to a minimum to reduce surface losses by radiation and convection, and the distance between the tube banks therefore makes effective descaling by mechanical methods impossible. Figure 10 shows tube nests in a boiler designed for 250 lb./sq. in.

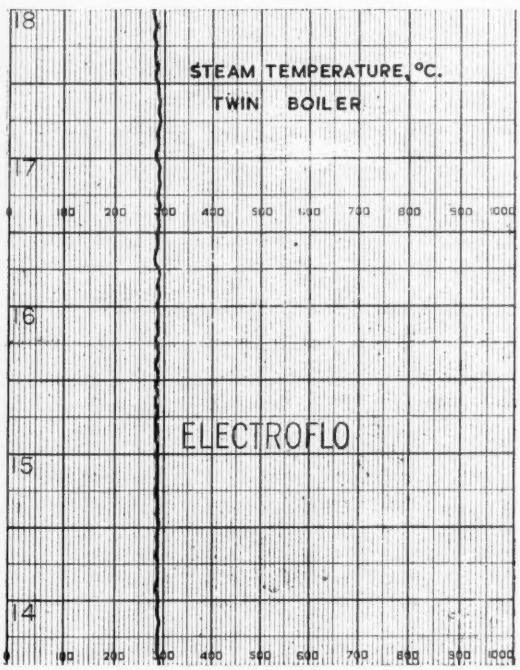


Fig. 9—Record of steam temperature from twin boiler when tubes are kept clean

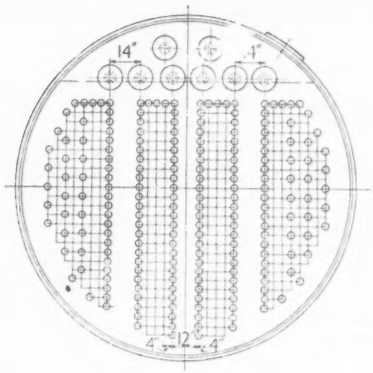


Fig. 10—Arrangement of tube nest for steam at 250 lb./sq. in. (end elevation on front end)

Correct feed-water treatment is the only means whereby the water surfaces can be kept clean. Analysis of the available raw-water supply will determine the choice of the treatment plant. Where the unit is manually controlled, routine testing to prevent unsoftened water passing into the feed system is of primary importance. In addition to the normal tests taken from the softening units, a continuous drip test should be taken from the feed-water recording tank or other suitable point and analysed each day to check if there is any hardness in the water passing to the feed-pump suction and therein to the boilers. Raw water should be tested every morning for hardness. With the base exchange system this procedure is necessary to determine the approximate amount of raw water that can be softened before regeneration of the units. The time between regenerations is dependent on the flow of water and its initial hardness and, if it is manually controlled, strict attention must be given to testing towards the end of a softening period, as complete failure of the reactions in the Zeolite can take place in less than an hour. In other words, softened water can be discharged from the unit during an estimated period, but if testing is neglected near the end of that period, hard water could be discharging within an hour.

Further treatment of the softened water is necessary. A definite alkalinity should be maintained by the addition of caustic soda and should be between *p*H 8·0 and 8·5. To counteract any possibility of caustic embrittlement it is necessary to dose the water with other chemicals, such as sodium sulphate, and it is recommended that this be added in certain ratios to the alkalinity, varying with the boiler pressures. With manual control and where the attendant has other duties, it is inevitable that a percentage of only partially softened water will sometimes pass to the boilers, and it is advisable to have additional treatment which will eliminate scale formation in the boilers. Phosphates can be used as additional treatment. The solution must be fed to the boiler in shots at specified intervals. These shots can be fed through the feed lines where the water temperature is 93·3° C. or lower, but where the temperature is high (148·8° C

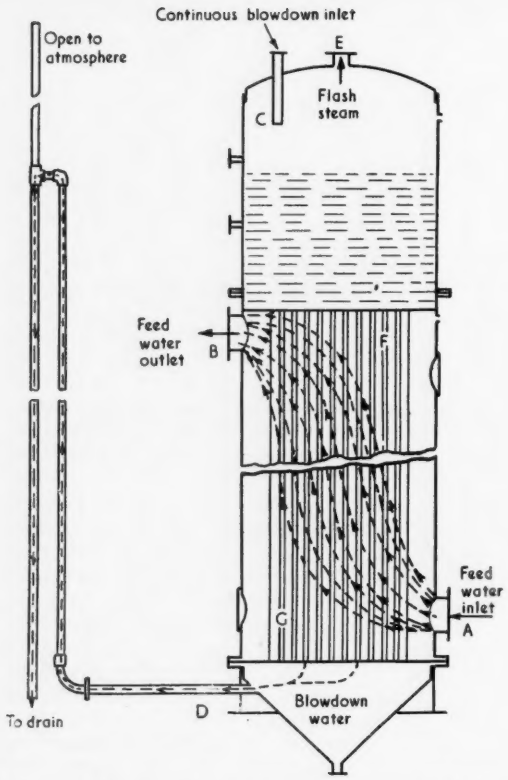


Fig. 11—Arrangement of blow-down heat exchanger

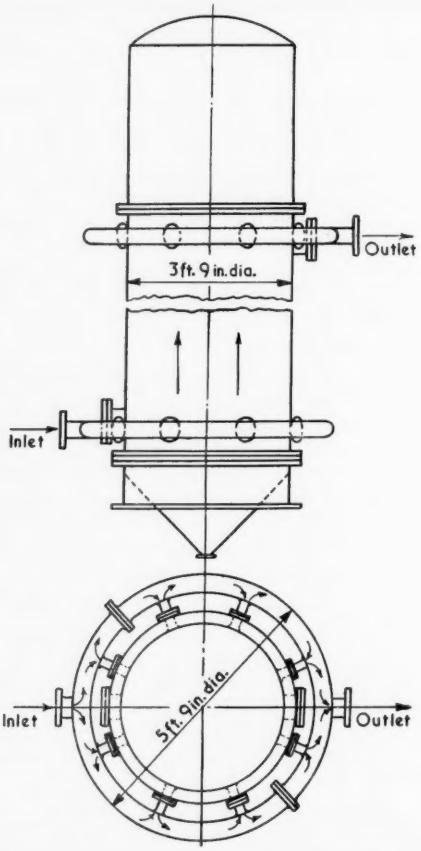


Fig. 12—Arrangement of header pipes on blow-down heat exchanger

and over), the solution must be injected straight into the boiler, otherwise the phosphates will decompose to some extent and form calcium phosphate deposits in the feed lines.

The boiler-water composition should be tested at regular intervals to maintain alkalinity and density within the correct limits. Concentrates can be controlled by the installation of a continuous blow-down system, which discharges into a tubular heat exchanger in circuit with the inlet water to the feed tank, thereby recovering the heat in the blow-down water.

Blow-Down Heat Exchanger

Figure 11 shows an arrangement of a typical heat exchanger. Feed water enters at *A* and discharges at *B*. Blow-down water enters at *C*, flows down through the tubes, and discharges at *D*. Flash steam discharges at *E* to the feed tank. On examination of a heat exchanger of this type it was found that the feed-water circulation was as shown by the arrows. Pitting and ' holing ' due to corrosion was experienced after a year in operation, and this was more severe at the relatively stagnant areas *F* and *G*. Corrosion is evident on the outer surfaces of the tubes only, the inner surfaces remaining in perfect condition. Header pipes with suitable connections fitted, as shown in Fig. 12, give improved water circulation and more efficient heat transfer. With similar conditions of feed-water flow and blow-down, the outlet temperature can be about 5·5° C. higher. Pitting due to corrosion is less severe and is more general. In Dalzell works there are two heat exchangers of this type; both were re-tubed at the same period in 1951, but header pipes were fitted to one only. The exchanger

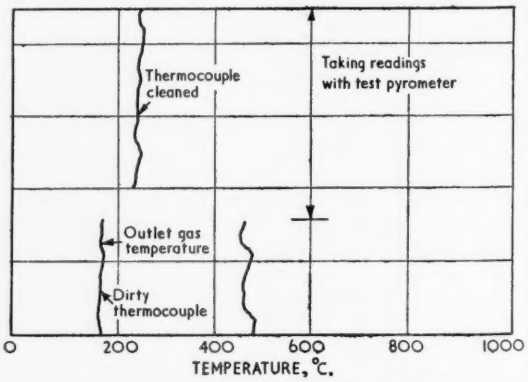


Fig. 13—Temperature chart showing dirty and clean thermocouple

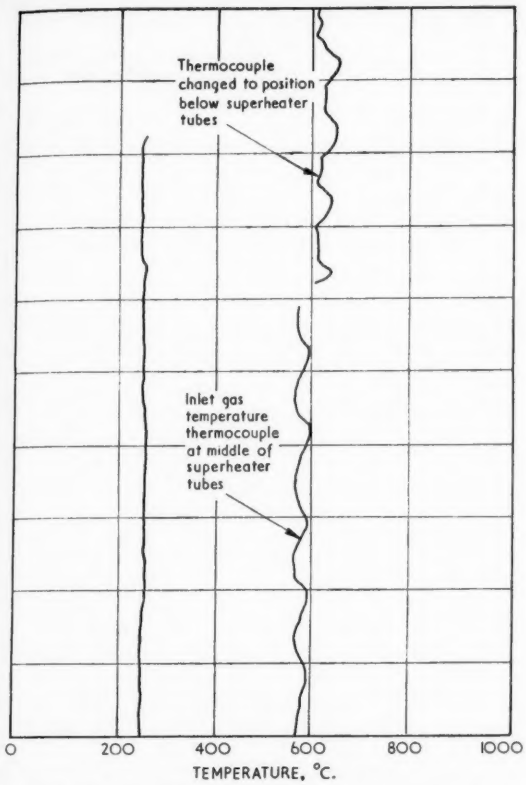


Fig. 14—Temperature chart showing thermocouple at middle of and below superheater tubes

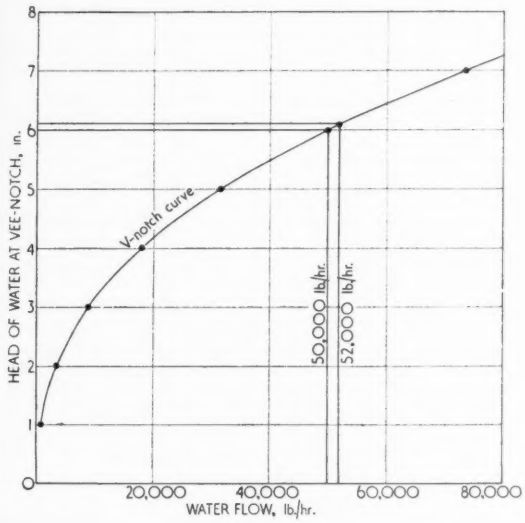
without the header pipes has had four tubes plugged-off within 18 months, whereas the exchanger on which header pipes are fitted is still operating efficiently. There is evidently continuous oxygen release on the outer surfaces of tubes where the temperature zone is higher than the average outgoing water temperature.

De-aeration cannot be effected at this stage. Tubes manufactured with an outer thickness of non-corrosive metal would give a considerably longer period in operation.

Accuracy of Measuring Instruments

The correct gas-temperature drop through the boiler and the water evaporated are most important for calculating the gas weight entering the boiler. Gas-temperature recorders should be checked with a reliable test instrument, and must be given regular inspection and maintenance. Thermocouples must be withdrawn at regular intervals and the outer surface cleaned, otherwise readings will be inaccurate. Figure 13 shows the importance of clean thermocouples. At the inlet end of the boiler the thermocouple should be inserted in the gas stream at a point before there is any heat transferred through the superheater tubes. Figure 14 shows the recorded difference in temperature when the thermocouple is inserted at the middle of the superheater tubes and then changed to a point below the tubes. The positions of the two thermocouples are shown in Fig. 8.

If the water to the boiler is measured by a **V**-notch recording instrument, it is essential for accurate flow measurement that the zero on the gauge measuring the depth of the water passing through the **V**, the zero on the recording drum, and the zero on the chart should all correspond to the exact level at the bottom of the **V**. If not properly adjusted the three zeros on the instrument can all be showing correct, and yet the water level could be either above or below the zero on the **V**. Figure 15 shows the curve for a **V**-notch recording instrument; reference to this curve shows that when the instrument gauge indicates 6 in. the flow recorded would be 50,000 lb./hr., but if the water level at the notch is actually 6·1 in. when the gauge indicates 6 in., the correct flow is 52,000 lb./hr.



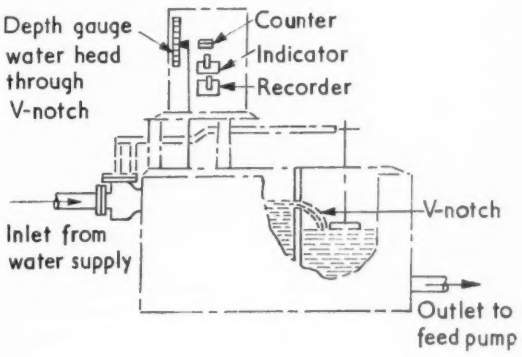


Fig. 15—V-notch curve and arrangement of tank

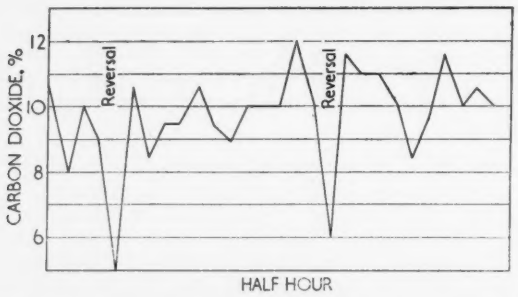


Fig. 16—Carbon dioxide readings taken approximately every minute over ½ hr. : end of test, no doors opened, fuel and air constant

Meters that indicate water or steam flow by the differential pressure through an orifice plate must also have the zero set correctly and all air must be removed from the piping system. When measuring steam, the correct pressure, temperature, and maximum flow should be given, so that an accurate calculation can be made to determine the orifice-plate bore.

Carbon Dioxide Measurement

The CO_2 content of the waste gases from open-hearth furnaces is very difficult to measure accurately for any prolonged period on a recording instrument. The quantity of dust borne with the gases is such that the filter is continually becoming choked and gas samples do not pass to the instrument. Where the gases are drawn by a water aspirator the supply must be clean and filtered. Even with an efficient filter small particles of grit pass to the small jets and again samples do not pass to the instrument. Industrial CO_2 recording units are not completely reliable and require excessive maintenance.

In open-hearth practice the CO_2 is very variable, depending on the reactions within the furnace bath, quite apart from fuel and air input. Figure 16 shows CO_2 readings taken by a portable tester approximately every minute over ½ hr., when fuel and air input were constant and the furnace doors were kept closed. On all tests a reliable portable tester should be used. A bulb aspirator should always be held vertically when taking samples. The valves have no springs, so that when the bulb is held horizontally they do not seat properly and a portion of the gas sample is pumped back into the flue.

Evaporation Tests

To obtain the correct gas-temperature drop through the boiler tubes the inlet and outlet casing should be tested for air infiltration when they are connected to boiler end-plates. This can be checked with a duck lamp and any leaks can be sealed off with asbestos rope thoroughly caulked in. With the end casing airtight the CO_2 percentage will remain constant through the tubes, and it is then possible from the CO_2 and temperature readings at the induction-fan inlet to calculate the exit gas temperature leaving the tubes. The CO_2 and gas temperature at the inlet to the fan will be lower than at the exit from the boiler

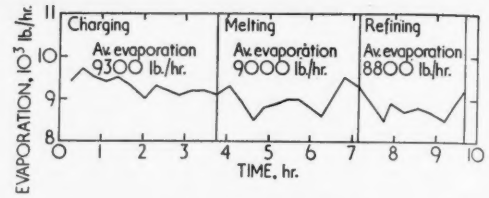


Fig. 17—Evaporation varying throughout charge (gauge glass test); period of test 9 hr. 40 min.

tubes, owing to air infiltration through the tube cleaning caps. When the gas-temperature drop through the tubes is checked by calculating from Fry's empirical formula[5] the inlet gas temperature used in the calculation will be the inlet temperature at the inlet products chamber less the temperature drop through the superheater tubes. For accurate individual boiler tests the steam meter should be used, provided that the orifice-plate bore has been correctly calibrated from the steam conditions.

Water meters normally record the total flow to all the boilers and, unless the pipe arrangement is suitable, it is not always possible to take the flow to an individual boiler. In addition, where the continuous blow-down system is in use, the percentage of blow-down must be deducted to assess the steam generated. This percentage can never be accurate, owing to the fluctuating evaporation obtained from the changing temperature and gas-weight conditions from an open-hearth furnace.

In an installation where the total water flow is recorded and individual steam meters are not fitted, an accurate evaporation test can be taken on one boiler by gauge-glass measurement, provided that the steam pressure is constant and the water level does not fluctuate. Taking a measurement 1 in. above and 1 in. below the normal working level, the weight of

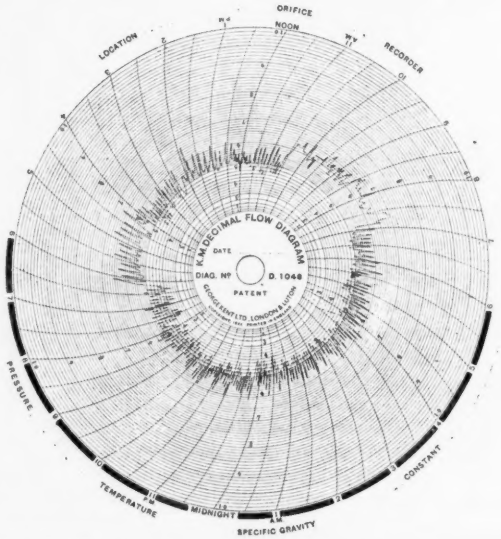


Fig. 18—Evaporation varying throughout 24 hr. (steam chart)

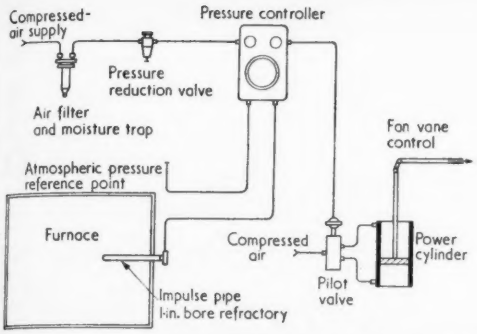


Fig. 19—Diagrammatic arrangement of furnace roof-pressure control system

water contained in this area is calculated at the temperature corresponding to the boiler pressure. The time taken for the water level to drop 2 in. with the check valve closed is noted, and also the time to rise 2 in. with the check valve open. The amount of water added for the complete cycle is calculated. This procedure is continued throughout the test period. The continuous blow-down valve must be closed during the test.

The author has taken many tests by this method over the total time from tap to tap, and also with the continuous blow-down open to ascertain the approximate percentage blow-down. Figure 17 shows how the evaporation can vary throughout the charge. Where a steam meter is fitted, similar fluctuations are shown on the recorded chart. Figure 18 shows evaporation varying throughout 24 hr.

Control of Furnace Roof Pressure

For efficient combustion conditions within the open-hearth furnace, control of roof pressure at a value

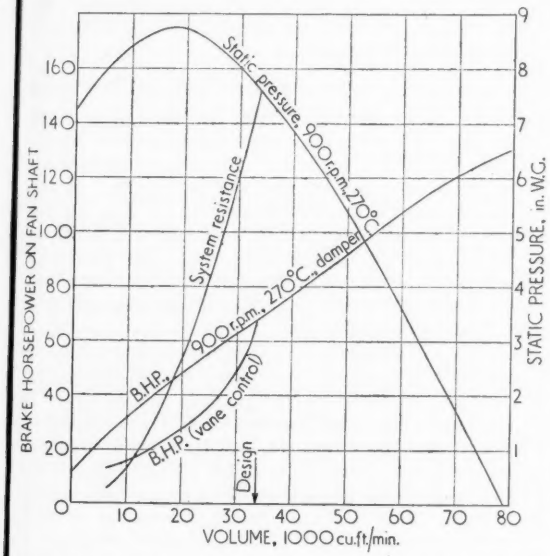


Fig. 20—Brake horsepower characteristics for damper and vane control

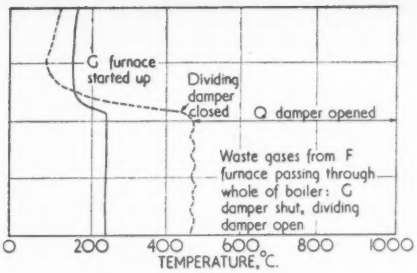

G furnace started up
Dividing damper closed
Q damper opened
Waste gases from F furnace passing through whole of boiler: G damper shut, dividing damper open
TEMPERATURE, °C.

Fig. 21—Temperature conditions when starting up cold furnace through twin boiler while other furnace is operating

which maintains approximately atmospheric level at door sills is essential. In a furnace that is not controlled the waste-gas flow for any particular fan speed remains constant, irrespective of variations in fuel supply or combustion air. This applies even to well-constructed furnaces and is a measure of the infiltration which can take place within the waste-gas path.

The furnace roof pressure can be controlled by one of the following methods:

(i) Controlled floating damper on inlet flue
(ii) Fixed-speed motor on the induced-draught fan with automatic damper control in the fan outlet duct
(iii) Variable-speed motor on the induced-draught fan
(iv) Fixed-speed motor on the induced-draught fan with automatic vane control fitted on the fan inlet.

The first three methods are standard practice on open-hearth melting furnaces, and the first two give excellent results. The fourth method has recently been adopted on one fan in the Dalzell works. The vanes are operated by a Hagan Servomotor using air at a pressure of 80 lb./sq. in. as the power medium and air pressure at 50–10 lb./sq. in. for the control medium, the position of the piston being dependent on the control pressure. The Servomotor acts in response to variations in the control pressure sent out by the furnace roof-pressure controller. The unit has not been in operation long enough to comment on any observations.

Figure 19 shows a diagrammatic arrangement of the furnace pressure-control system. The curves in Fig. 20 show the b.h.p. characteristics for damper and vane control.

Starting up Furnaces from Cold

The normal practice is to apply a heater to the furnace before oiling or gassing. When oiling or gassing, the furnace is draughted straight through the boiler. This does not present any difficulty with a single boiler, provided that the water is thoroughly heated and the pressure gauge shows a slight pressure. In a twin boiler, however, there are disadvantages in draughting a relatively cold furnace through one half while the other is passing gases probably up to 600° C. The main disadvantage is unequal expansion on the tube plates, which can cause tube-end leakage. Figure 21 shows the temperature conditions when starting up a furnace from cold through one half of a twin

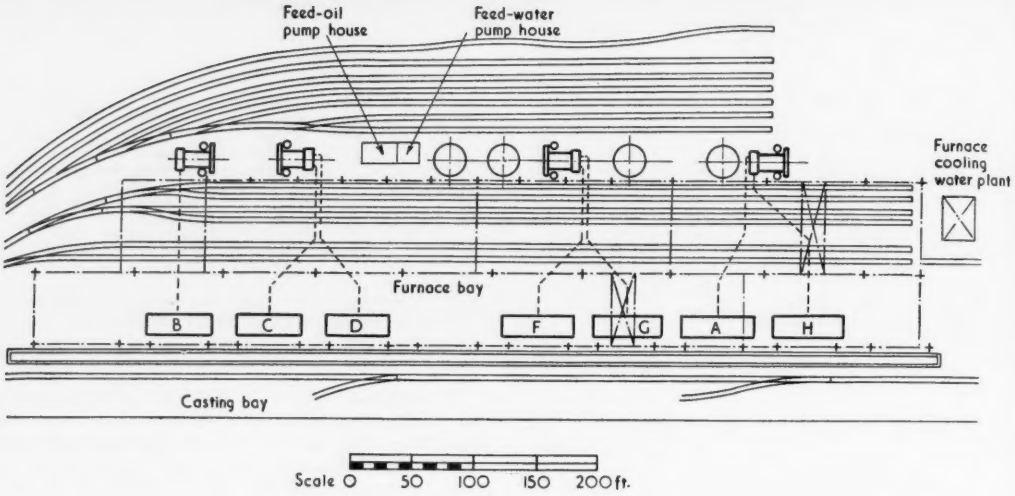


Fig. 22—Layout of plant

boiler, while the other furnace is on normal operation through the other half of the boiler.

Auxiliary Firing Unit

Where pitch-creosote is the fuel fired to the furnaces it is necessary at holiday periods to keep the steam passing through the tracer lines and to circulate the pitch-creosote continuously at a temperature of not less than 26·6° C., otherwise the pitch hardens. An oil burner of sufficient capacity to generate at 40–50 lb./sq. in. can be arranged in the inlet products chamber of a single boiler.

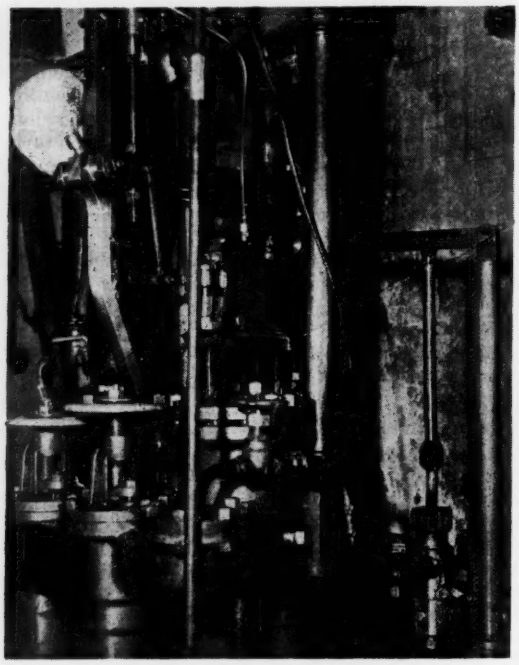


Fig. 23—Auxiliary chemical pump

Routine Examination

All fittings and mountings on the boiler should be thoroughly examined by a competent engineer. Stop valve, blow-down, and check valve seats should be checked for tightness. Safety valves and seats should be given special attention. Valves must be free to float on spindles to ensure tight seating. Tube ends should also be examined for leakage.

Internally, the discharge from the extended feed pipe should face toward the inlet tube plate and set to discharge slightly downward. The boiler shell should be examined along the water level for any sign of corrosion. If there is any scale formation on the tubes a sample should be kept for comparison at the next examination.

Evaporation in Fire-Tube Boilers at Higher Pressures

In the plant described later in the paper three boilers are generating at a pressure of 145 lb./sq. in. and one at 250 lb./sq. in. and it is of interest to compare the evaporation at the two pressures. If the gas-temperature drop is calculated by the Fry log–log formulæ, it will be seen that, for equal conditions of tube area and tube length, the gases from the high-pressure boiler will exhaust at a considerably higher temperature than one at a lower pressure, and heat transfer is diminished.

The mean temperature of the tube wall is taken as the saturation temperature, which at 145 lb./sq. in. is 184·4° C. and at 250 lb./sq. in. is 207·8° C.

Assuming a gas temperature of 605° C. at the boiler tube inlet and gas weight of 70,000 lb./hr. and calculating the temperature drop at 145 and 250 lb./sq. in. it is found that the gas temperature at the tube outlet is approx. 19·4° C. higher when generating at 250 lb./sq. in. where tube area and tube length are similar. In practice, the exit gas temperature is found to be about 25° C. higher, and at the inlet temperature and

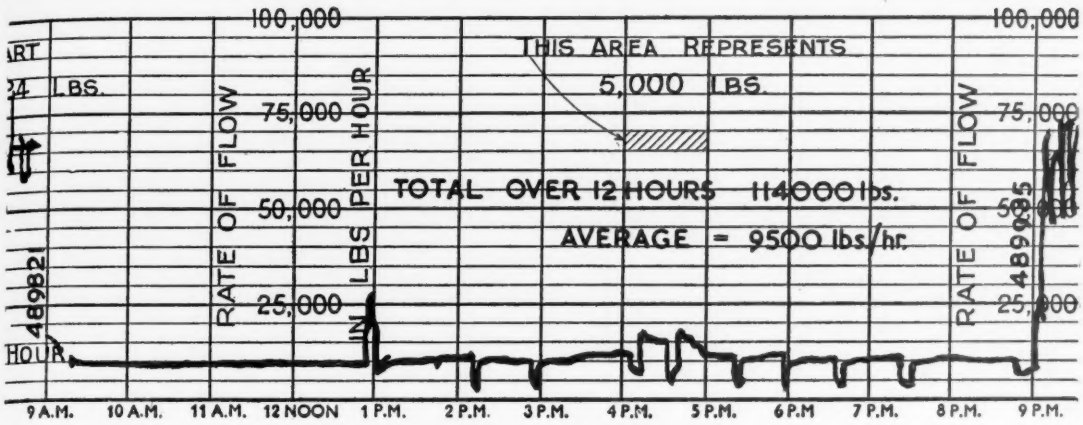


Fig. 24—Evaporation during test period

gas weight given, the evaporation is reduced by about 800 lb./hr.

DESCRIPTION OF BOILER PLANT IN OPERATION WITH OPEN-HEARTH FURNACES

The melting shop consists of seven 70-ton nominal basic furnaces, four of which are fired with pitch-creosote and three with heavy fuel oil. The plant is laid out for producing steel for the structural shipbuilding and general engineering industries.

Four waste-heat boilers are installed, all of the Cochran Sinuflo fire-tube type. Three of the boilers operate as twin units, two furnaces operating through one boiler, and the exhaust gases from each furnace pass through one half of the boiler, which is divided at the inlet and the outlet products chamber. Each boiler has two induced-draught fans giving individual control to each furnace. The fourth boiler operates in conjunction with one furnace only. All boilers have the same dimensions, heating surface, and tube area. Figure 22 shows the layout of the plant. Boiler particulars were as follows:

Length over tube plates	15 ft. 8 in.
Dia. of shell	12 ft. 6 in.
Sinuflo tubes:	
Number	344
External dia.	2½ in.
,, heating surface	3480 sq. ft.
Internal ,, ,,	3040 sq. ft.
Stay tubes:	
Number	210
External dia.	2½ in.
,, heating surface	2130 sq. ft.
Internal ,, ,,	1600 sq. ft.
Area through tubes:	
Sinuflo	8·95 sq. ft.
Stay	4·03 sq. ft.
Total	12·98 sq. ft.
Designed working pressure	250 lb./sq. in.
Induced-draught fans:	
Capacity	33,750 cu. ft./min.
Gas temperature	270° C.
Press W.G.	7·6 in.
R.P.M.	600–900
Horsepower	28–75
Current supply	108–280 amp. 230 V. (D.C.)

Steam from two of the double boilers and the single boiler generated at 145 lb./sq. in. is discharged into a common main and is primarily used for atomization on six furnaces. Excess steam passes through an overflow valve and is discharged into the 100-lb./sq. in. works' ring main. The other double boiler generates steam at 250 lb./sq. in. and atomization is used at this pressure on the seventh furnace. The excess steam passes through an overflow valve into the 145-lb./sq. in. main. Two vertical-ram pumps are in continuous operation, one for 250 lb./sq. in. and the other for 145 lb./sq. in. A rotary pump acts as a standby. The discharge piping is arranged so that either of the vertical-ram pumps can operate at 250 lb./sq. in. The exhausts from all steam pumps pass through coils in the feed tank. The continuous blow-down discharges into a tubular heat exchanger in circuit with the inlet water to the feed tank, the flash steam passing into the feed water in the tank.

The boiler-water level is controlled by regulators. Feed water is measured by a recorder unit which measures the water flow to all the boilers. A steam meter is installed on the boiler operating at 250 lb./sq. in. Gas and steam temperatures are recorded on electro-flow instruments. Feed temperature is recorded by a Rototherm unit. Draught conditions are indicated by manometers.

The feed water is softened by the Neckar base exchange system and, after softening, a definite alkalinity is maintained by the addition of caustic soda. Sodium sulphate is also added to counteract any possibility of caustic embrittlement. At the feed-pump inlet, water is dosed with a phosphate mixture which in solution is injected in shots once each shift. This addition gradually removes any scale formed on the tubes and prevents further scale formation.

At the pressure of 145 lb./sq. in. the sulphate/carbonate ratio is maintained at a little over 1 : 1, but at the pressure of 250 lb./sq. in. a 3 : 1 ratio is maintained. The additional chemicals in solution necessary to maintain the 3 : 1 ratio are added at the feed-pump suction by a small auxiliary pump connected to the feed-pump crosshead. This pump is designed to discharge about 4 gal./hr. at average speed of the feed pump. Figure 23 shows the auxiliary pump designed by the author.

Typical Test on Single Boiler (Furnace Fired with Pitch-Creosote)

This test was taken throughout a complete furnace charge over 12 hr. The continuous blow-down was closed during the test and the water evaporated was recorded and fed to the boiler through an independent feed line. Figure 24 shows the chart recording. Inlet and outlet gas temperatures were checked with a mercury-in-steel pyrometer. Carbon dioxide readings were taken with a CO_2 indicator. The pitch-creosote consumption was recorded on a flowmeter.

Pitch-Creosote Composition

Carbon, wt.-%	90·0
Hydrogen, wt.-%	6·0
Oxygen, wt.-%	2·4
Nitrogen, wt.-%	1·0
Sulphur, wt.-%	0·6

The specific gravity is 1·117 and the calorific value is 16,600 B.Th.U./lb.

Combustion of One Gallon with No Excess Air

Oxygen required, cu. ft.	379
Nitrogen accompanying oxygen, cu. ft.	1424
CO_2 in waste gas, cu. ft.	318
H_2O in waste gas, cu. ft.	201
Maximum CO_2, %	18·2

Test Measurements

Boiler pressure	145 lb./sq. in.
Steam temperature (av.)	276·6° C. = 1288 B.Th.U./lb. (Callendar Steam Tables, 1939)
Feed-water temperature (av.)	65·5° C. = 118 B.Th.U./lb.
B.Th.U.'s added per lb. of steam	1170
CO_2 exit from checker (av.)	12·5% = 44% excess air
CO_2 inlet to boiler (av.)	10·5% = 70% excess air
CO_2 inlet to fan (av.)	10·0% = 79% excess air

Gas temperature exit from checker		780° C.
,, ,,	inlet to boiler (av.)	632° C.
,, ,,	inlet to fan (av.)	240° C.
,, ,,	outlet from boiler (calculated)	254·4° C.

Pitch-creosote consumption (av.)	280 gal./hr.
Average evaporation	9500 lb./hr., 11,450 lb./hr. (' from and at ')
Factor of evaporation	1·205
Draught inlet to boiler (av.)	0·9 in. W.G.
Draught inlet to fan (av.)	2·0 in. W.G.

Estimate of Heat Balance

Heat Input (all values in therms/hr.)

Potential heat in oil	520·0
Sensible heat in oil	2·2
Sensible heat in steam	13·7
Total	535·9

Total heat input	535·9	
Heat at boiler exit	74·3 =	13·9%
Heat to furnace, boiler, and all losses	461·6 =	86·1%
Total heat input	535·9	
Heat at checker exit	214·0 =	40%
Heat absorbed in furnace and checkers	321·9 =	60%
Heat at checker exit	214·0	
Heat at boiler inlet	192·0	
Heat loss between checker exit and boilet inlet	22·0 =	10·3%
Heat available for steam	192·0	
Heat added to steam	111·0 =	57·8%
Heat drop through boiler	81·0	
Heat at boiler exit	74·3 =	38·7%
Heat loss by radiation	6·7 =	3·5%
Total heat input	535·9 =	100%

Heat Distribution

Heat absorbed in furnace and checkers	321·9 =	60·0%
Heat added to steam	111·0 =	20·7%
Heat loss, checker exit to boiler inlet	22·0 =	4·15%
Heat loss, radiation in boiler	6·7 =	1·25%
Heat loss at boiler exit	74·3 =	13·9%

(No allowance has been made in this heat balance for intrinsic heat from bath reactions.)

Heat loss at boiler exit from Siegert's formula, %

$$= \frac{0{\cdot}34(T-60)}{10{\cdot}5} = \frac{0{\cdot}34(490-60)}{10{\cdot}5}$$

$$= 13{\cdot}9\%$$

Boiler extraction efficiency, %

$$\frac{T_1 - T_2}{T_1 - T_s} = \frac{1170-490}{1170-364} = 84{\cdot}5\%$$

Data Derived from Test

Furnace:

Steel produced	84 tons 10 cwt.
Pitch-creosote consumption	3360 gal.
Gallons per ton of steel	39·76

Boiler:

Steam produced	114,000 lb.
Steam produced per furnace-hour	9500; 11450 lb./hr. (' from and at 100° C.')
Steam produced per gal.	33·9 lb.
Steam produced per ton of steel	1350 lb.; 1625 lb. (' from and at 100° C.')

Coal Equivalent

Fuel boilers	7 lb. of steam per lb. of fuel
Coal equivalent per furnace-hour	1357 lb.
Coal equivalent per gal.	4·84 lb.
Coal equivalent per ton of steel	193 lb.

Calculation of Gas Weight

From Temperature Drop and Evaporation:

$$\text{Specific heat} \times 0{\cdot}965\,W\,(T_1 - T_2) = E \times \text{B.Th.U. added to steam}$$

$$0{\cdot}24 \times 0{\cdot}965\,W\,(1170 - 490) = 9500\,(1288 - 118)$$

$$W = \frac{9500 \times 1170}{0{\cdot}24 \times 0{\cdot}965 \times 680} = 70{,}000 \text{ lb./hr.}$$

From Fuel Composition:

Calculated from the fuel composition the gas weight per cu. ft. = 12·85 lb. The volume of the waste gases at 70% excess air is 3213·5 cu. ft./gal.

$$\text{Gas weight per hour} = \frac{280 \times 3213{\cdot}5}{12{\cdot}85} = 70{,}000 \text{ lb./hr.}$$

In practice the following formula[8] is sufficiently accurate to determine the gas weight:

$$\text{Gas weight per lb. of fuel} = \frac{\text{lower calorific value} \times \text{maximum } CO_2}{1280 \times CO_2 \text{ from gas analysis}}$$

This formula can be used for solid and oil fuels, but not for gaseous fuels.

From Formula:

$$\frac{16{,}600 \times 18{\cdot}2}{1280 \times 10{\cdot}5} = 22{\cdot}4 \text{ lb./lb. of fuel}$$

Gas weight = 280 × 11·17 × 22·4 = 70,000 lb./hr. (11·17 = lb./gal.)

The gas weight can also be calculated from the formula evolved by Rosin[7]:

$$9{\cdot}9 \frac{\text{lower calorific value}}{1000} = \text{cu. ft./lb. with no excess air.}$$

$$\therefore 9{\cdot}9 \times \frac{16{,}600}{1000} = 164 \text{ cu. ft./lb.}$$

$$\text{Gas weight per lb. of fuel} = \frac{164 \times 18{\cdot}2}{12{\cdot}8 \times 10{\cdot}5} = 22{\cdot}2 \text{ lb.}$$

The difference in the gas weight calculated by the two formulæ is less than 1%.

Further Heat Recovery

The author has recently investigated the possibility of additional heat recovery from the boiler exit gases by passing them through a further heat exchanger and transferring heat units to the boiler feed water.

In the twin boiler, which operated at a pressure of 145 lb./sq. in. and a feed temperature of 71·1° C., the average evaporation was 17,000 lb./hr., but since the pressure was raised to 250 lb./sq. in., the average evaporation is now 15,500 lb./hr., operating under similar conditions.

Raising the feed temperature from 71·1° to 165·6° C. by heat transfer through an economizer would increase the evaporation by 18% to 18,300 lb./hr., with a gas fall of 48° C., assuming similar gas weight and no radiation losses.

The average steam temperature is 260° C., the heat added to the steam with the feed at 71·1° C. is 1134 B.Th.U., and the heat added with the feed at 165·6° C. is 961 B.Th.U. Heat units transferred will be the same, so that 15,500 × 1134 = new evaporation × 961, and the new evaporation would be 18,300 lb./hr., equivalent to 18% increase.

The gas weight at the economizer inlet is about 146,000 lb./hr., and the temperature fall through the economizer would be about 0·25 × 146,000 × fall = 18,300 (301–128), equal to 48° C. The gas temperature at the fan inlet averages 276·7° C. and exit temperature from an economizer would be about 228·3° C. Under operational conditions the exit

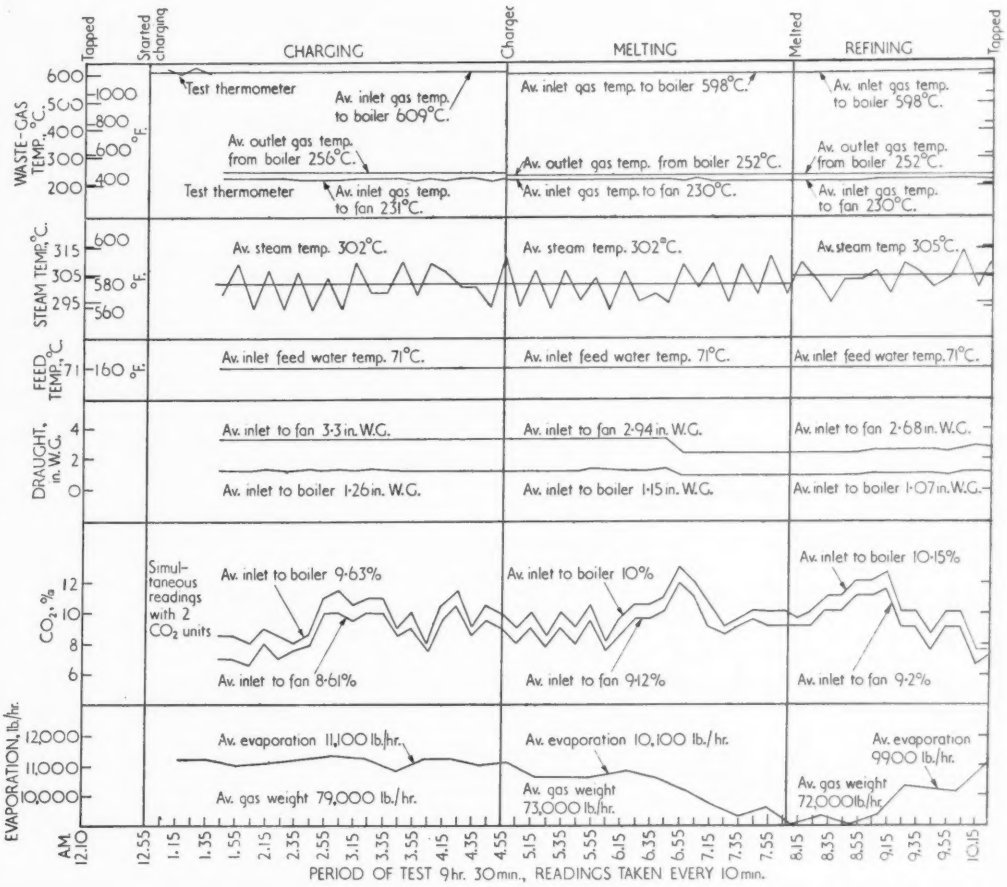


Fig. 25—Conditions at boiler during charging, melting, and refining

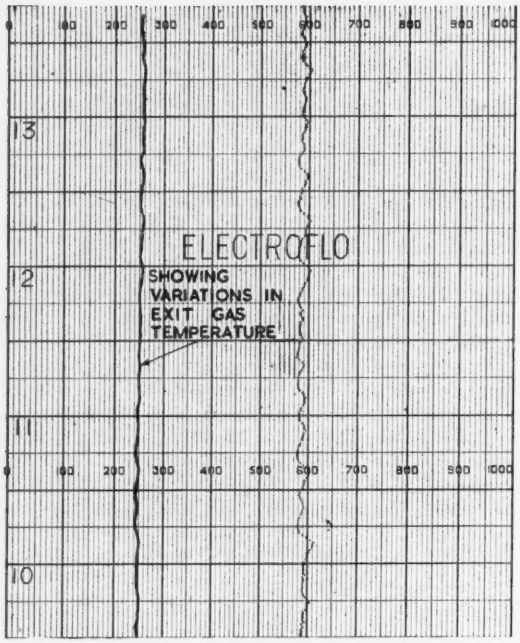


Fig. 26—Boiler exit gas-temperature conditions

temperature would be lower. The main conditions affecting the installation of an economizer for heat recovery at low temperature from an open-hearth furnace are as follows:

(i) Size of unit required for the necessary temperature drop
(ii) Initial cost of the complete installation
(iii) Increase in evaporation and equivalent fuel saving
(iv) Possibility of steaming in the economizer
(v) Induced-draught fan power
(vi) Cleaning
(vii) Composition of flue dust passing to the economizer
(viii) Minimum temperature of gases at the economizer exit.

Size of Unit—Numerous tests were taken at various periods of furnace operation and under different operational conditions to ascertain maximum and minimum gas weights and variation in gas temperature at the induced-draught fan inlet. Evaporation tests over charging, melting, and refining periods showed an average fluctuation in gas weight of about 7000 lb./hr. between charging and refining. Figure 25 shows the conditions when charging, melting, and refining. Under normal conditions the inlet gas temperature to the fan varies from 5° to 10° C. Figure 26 shows normal exit-temperature conditions. To keep the economizer outlet water from exceeding the specified limit corresponding to the working pressure, the economizer must be designed for average conditions.

Initial Cost—The cost of the complete installation must be such that it can be completely repaid in not more than two years.

Increase in Evaporation and Equivalent Fuel Saving—The equivalent cost of fuel saving resulting from the increased steam production less operational costs should be carefully estimated to ensure the repayment of capital cost within two years.

Steaming in Economizer—Evaporation in the boiler is continuous throughout furnace operation and, where a constant steam pressure is maintained by an automatic overflow valve which releases excess steam produced into a lower pressure main, the flow of steam from the boiler is not restricted. Water would therefore be passing continuously through the economizer. If the inlet gas temperature to the boiler rises, the evaporation increases and more water passes through the economizer. The boiler exit-gas temperature is found to rise about 15–20° C. with a sudden sharp increase in inlet temperature, as sometimes results from charging oily scrap to the furnace or charging hard limestone to the hot bath. Figure 27 shows the rise in temperature when a box of hard limestone is charged. The danger of steaming appears to be remote if the economizer is correct in size and design.

Induced-Draught Fan Power—Information was obtained from the fan makers about the operation of the induced-draught fan at various temperatures; the figures supplied show that, owing to the reduction of gas volume by the fall in gas temperature, it is possible to operate with increased resistance through an economizer without increase in fan power, provided that the gas weight is not increased by air infiltration between boiler, economizer, and fan.

Cleaning—Owing to the almost continuous boiler cleaning, loosened dust products will pass to the economizer. The dust will be severe and must be removed by efficient blowers before it accumulates in quantity.

Composition of Flue Dust Passing to the Economizer—Samples were taken from flue dust deposited in the boiler tubes. The furnaces operating in conjunction with this boiler are fired with heavy fuel oil, which has a sulphur content of about 2½%. Sulphuric-acid attack appears possible as the acid may exist in small quantities in the gas stream. The small quantity of SO_3 in the gases can form acid films on the metal at temperatures above the water dew-point. The determination of the dew-point in exhaust gases has been

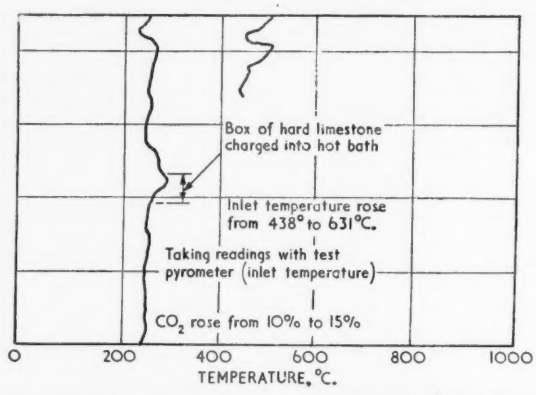


Fig. 27—Rise in temperature when charging a box of hard limestone into the furnace bath

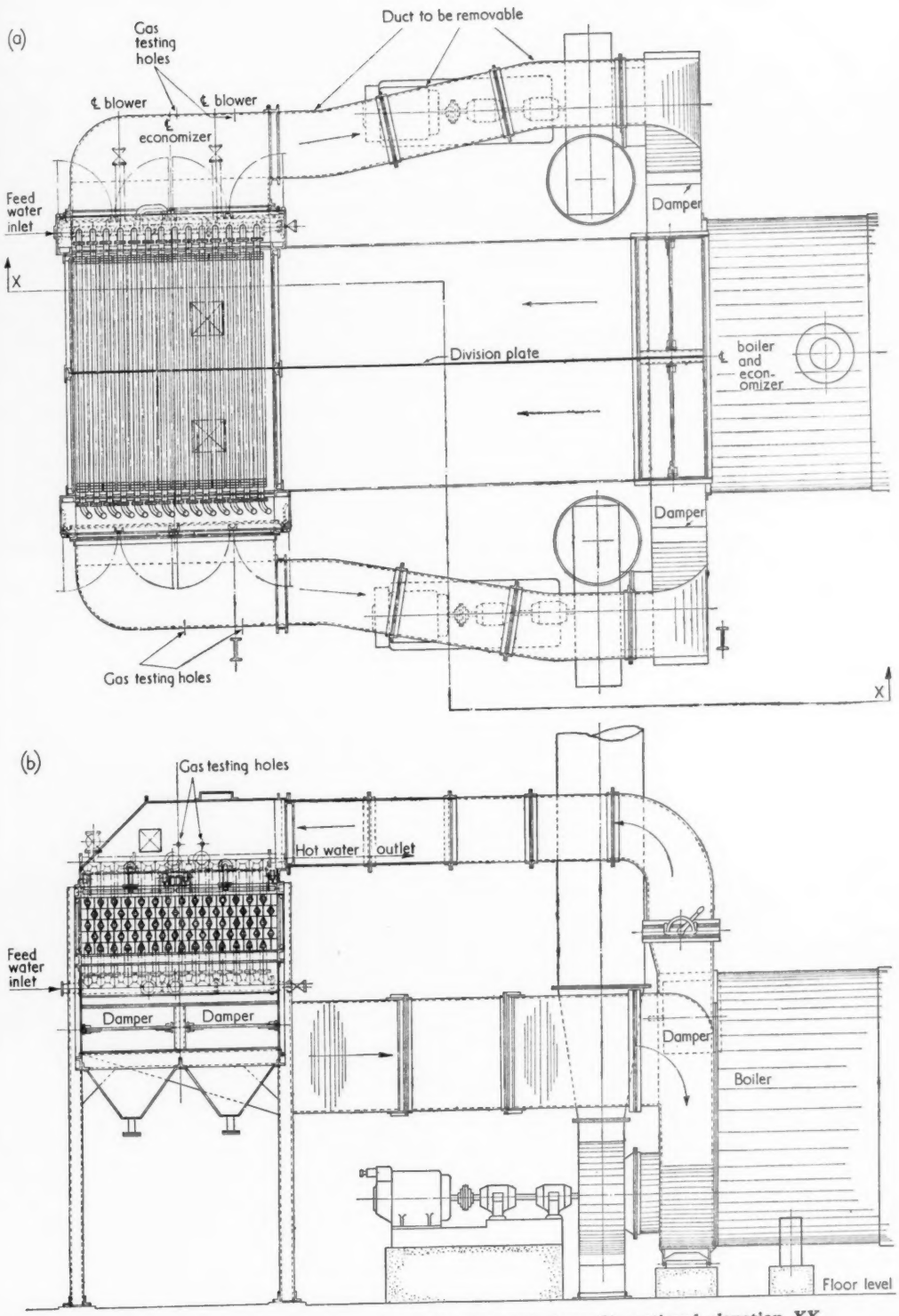


Fig. 28—Arrangement of economizer: (*a*) Sectional plan; (*b*) sectional elevation *XX*

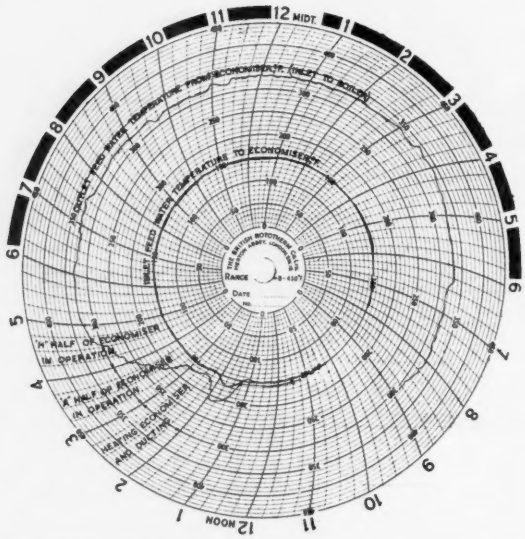


Fig. 29—Chart showing rise in feed-water temperature through economizer

thoroughly investigated by the B.C.U.R.A.; tests have proved the existence of an ' acid ' dew-point in gases from oil-fired furnaces. This acid dew-point appears at relatively high temperatures, varying with water and SO_3 content, usually in the range 93·3–148·9° C. The report on the boiler-tube deposit shows the following analysis:

Location	SO_3, %	V_2O_5, %
Inside bottom tubes (left-hand)	26·6	0·94
Inside bottom tubes (right-hand)	26·8	0·94
Inside centre tubes	49·8	1·56
Inside top tubes	20·6	1·67

The report states that the vanadium contents of the deposits are satisfactorily small, and also that the deposits examined do not suggest difficulty about removal from an economizer.

It appears that the tendency is for sulphuric acid in the gas stream to remain in the stream condensed on fly ash; it is discharged to atmosphere through the induced-draught fan. Severe corrosion is not expected if the exit temperature of the gases is higher than the maximum temperature at which the acid dew-point exists.

The feed-water temperature should be at least 71° C., so as to keep the metal temperature of the tubes well above the water dew-point (37·8° C.).

Minimum Temperature of Gases at Economizer Exit—As the acid dew-point appears in waste gases from oil-fired furnaces at temperatures up to 148·9° C., the exit gases from an economizer should not be lower than 176·7° C.

CONCLUSIONS

The results obtained from these investigations were discussed thoroughly and it was finally decided to install an economizer at Dalzell works on the boiler operating at a pressure of 250 lb./sq. in.

The economizer is of the gilled-tube type; the tube bank has 70 12-ft. tubes, 14 tubes wide by 5 high in one tier. On the gas side the tube bank is divided into two sections, and the gases pass from each half of the boiler through each half of the economizer to each induced-draught fan, ensuring independent draught control on both furnaces. The gas flow is one pass downwards, and dampers are arranged to control the flow over the full width of the tube bank. The water system is common to both sections of the economizer and the feed water fed into the bottom header at one end passes up through the tubes and is discharged through the top header at the opposite end. A centre damper is fitted on the underside of the tubes to permit the gases to pass to one fan if a furnace is off for repairs. A similar damper has been fitted on the boiler exit division plate to enable the gases from one furnace to be discharged through either fan, should the economizer be off. Figure 28 shows the economizer arrangement.

Acknowledgments

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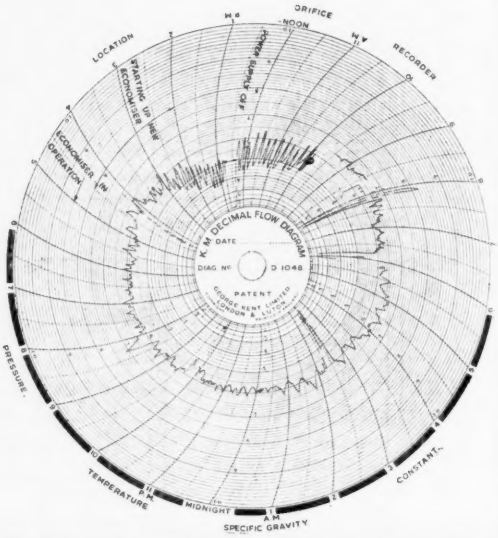


Fig. 30—Chart showing increase in steam produced as a result of economizer

APPENDIX

Economizer Operation

Instrumentation

Instruments used on the equipment include: pyrographs to record economizer inlet and outlet gas temperatures; a two-point recorder to record inlet and outlet feed-water temperatures; manometers to indicate draught loss through the economizer; a kilowatt-hour meter on each induced-draught fan motor, to integrate electrical unit consumption; and a high water-temperature alarm (set at 182·2° C.).

The new economizer was put into commission on Tuesday, 21st April, 1953, and Figs. 29–32 show actual recordings of the changes in operational conditions when the unit was started. The heating of the ducting and economizer was very gradual, and free movement due to expansion was checked at the ducting expansion joints before the total gas volume was allowed to pass through the economizer. The steady rise in feed-water temperature during this period is recorded in Fig. 29.

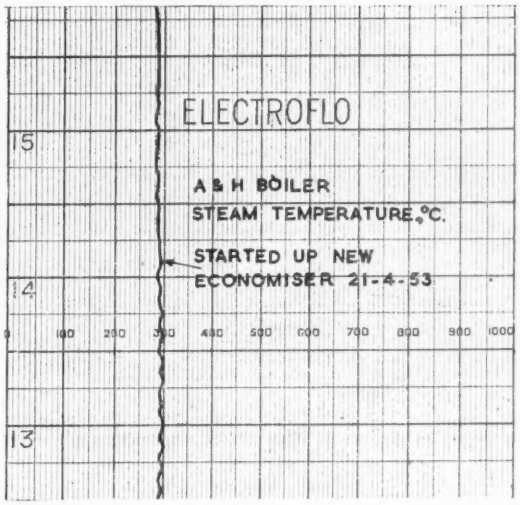


Fig. 32—Chart showing steam temperature

The increase in evaporation during the same period is shown in Fig. 30. This chart shows that the evaporation peaks are narrowed when the economizer is in operation. This is due to the difference in feed-water temperature entering the boiler. The saturation temperature at a pressure of 250 lb./sq. in. is about 207·8° C. and, when the boiler water level control valve opens and admits water at, say, 65·6° C., the water in the boiler is cooled and evaporation is lowered. Water entering the boiler at 165·6° C. has little effect on the boiler water temperature, and evaporation is steadier.

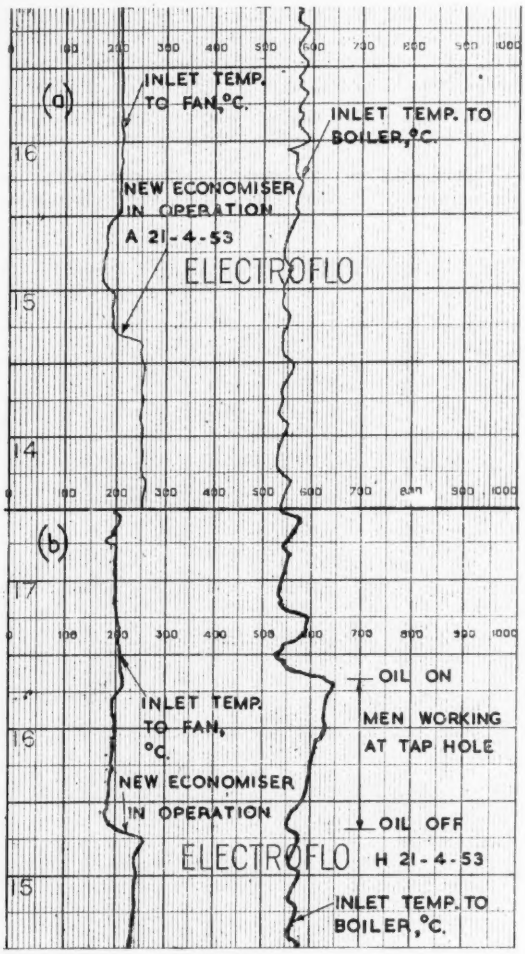


Fig. 31—Chart showing exit gas-temperature drop to (*a*) fan *A*, (*b*) fan *H*

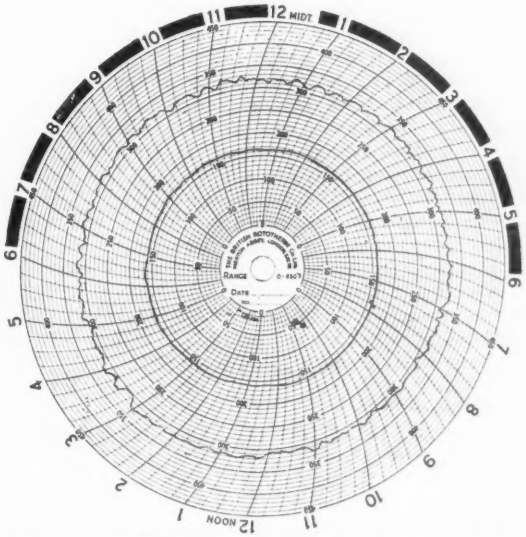


Fig. 33—Chart showing recorded feed-water temperatures after 288 hr. operation

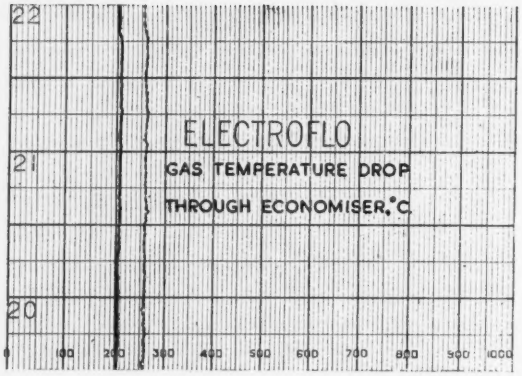


Fig. 34—Chart showing gas-temperature drop through economizer after 288 hr. operation

Figure 31 shows the gas-temperature drop through each half of the economizer, the discharge to atmosphere averaging about 255° C. without the economizer and about 200° C. with the economizer. Although the additional draught loss is about 0·75 in. W.G., the fan-motor horsepower remains practically the same.

The steam-temperature recording, shown in Fig. 32, emphasizes the improved steam conditions when feeding high-temperature water into the boiler. While the boiler was feeding before the economizer went into commission, the steam temperature is shown to fluctuate about 10° C., but it is almost constant when the economizer is operating.

The data obtained from Figs. 29–32 show the following information when the economizer is operating. The feed-water temperature rises from 65·6° C. to an average of 165·6° C. and, at the steam temperature recorded, this rise is equivalent to an 18% increase in evaporation. Average evaporation has increased from 15,500 to 18,300 lb./hr. The gas-temperature drop through the economizer is about 55° C.

Figure 33 is a chart recording of the feed-water temperatures after the economizer has been in operation for 288 hr. and shows a rise from about 71·1° C. to an average of 158·9° C., equivalent to an increase in evaporation of about 17%. The average evaporation over 24 hr. is 19,500 lb./hr. Figure 34 shows the gas-temperature drop through the economizer after the same period in operation.

Figure 35, which shows increase in evaporation with the economizer, is the average over every 8 hr. taken from steam-meter readings. Average evaporation without the economizer is 15,300 lb./hr. and the average with the economizer is 18,200 lb./hr.

Latest Operating Details

Since the paper was presented, the economizer described therein has been in almost continuous operation. Until the middle of July the two melting furnaces exhausting through the boiler and economizer were fired with heavy fuel oil, which has an average sulphur content of 2½%. At the beginning of August the furnaces were changed over to pitch-creosote

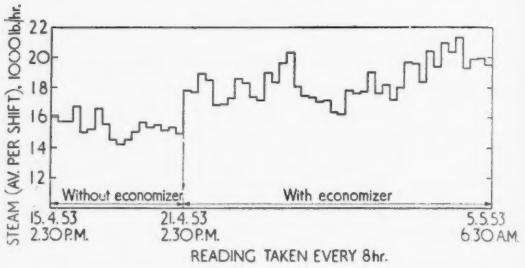


Fig. 35—Graph showing evaporation without and with economizer

firing; the average sulphur content of this fuel is 0·5%.

In July the economizer was by-passed after having been in continuous operation for 1870 hr. The main reason for by-passing the unit was to examine the condition of the heating surfaces, and the external condition of the tubes and gills was found to be good. There was no deposit at the 'hot end,' but a small amount of light deposit had collected at the 'cold end.' The composition of this deposit as ascertained by analysis is as follows:

SO_3, %	Cr, %	V_2O_5, %	SiO_2, %	CaO, %	Fe_2O_3, %
51·6	0·11	0·58	2·92	Nil	30

This should be compared with the composition of the sample of deposit taken from the boiler tubes

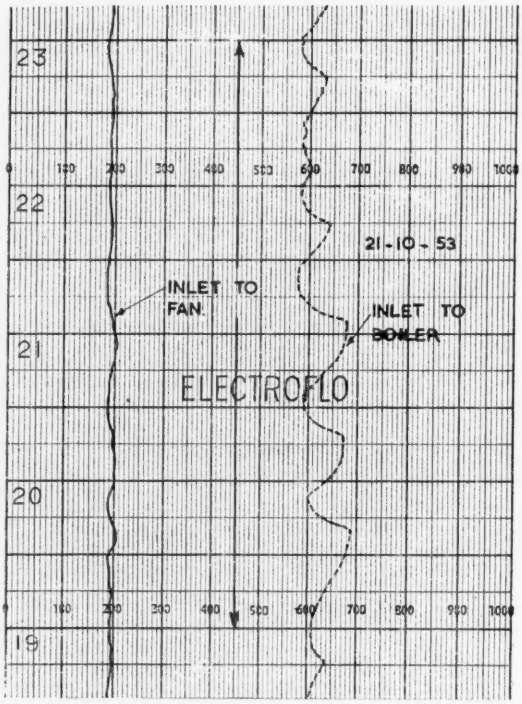


Fig. 36—Chart showing variations in inlet gas temperature to boiler

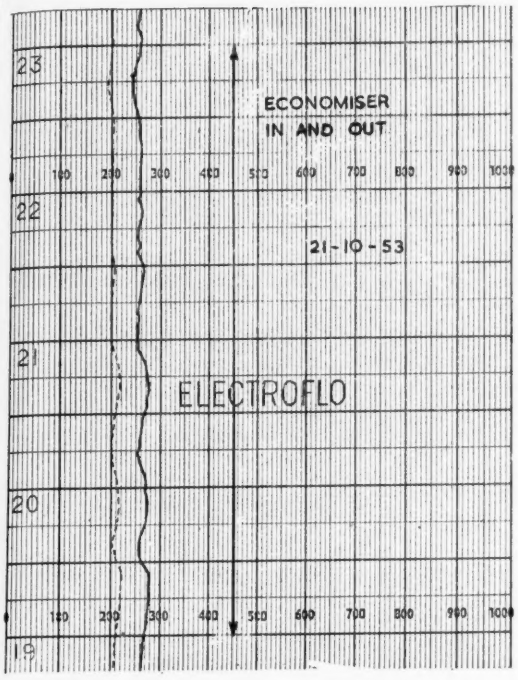


Fig. 37—Chart showing variations in inlet and outlet gas temperatures at economizer

(as shown in the paper), when a SO_3 content of 49·8% and a V_2O_5 content of 1·56% were found. The quantity of deposit at the 'cold end' was insufficient to affect the draught resistance through the economizer. Experiments were made to find the most suitable method of removing the deposit; it was found that washing with a fairly strong jet of water effectively cleaned the gills.

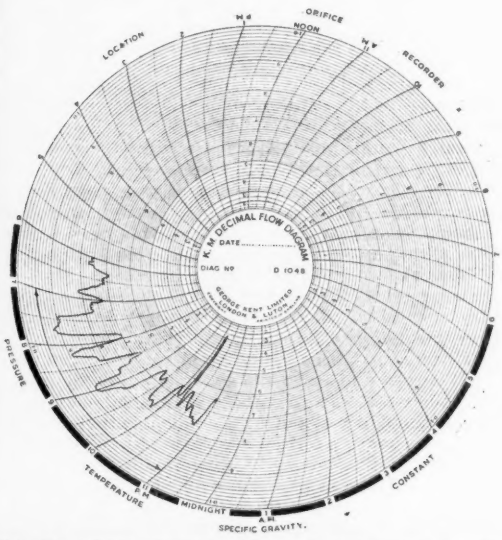


Fig. 38—Chart showing rise and fall in evaporation

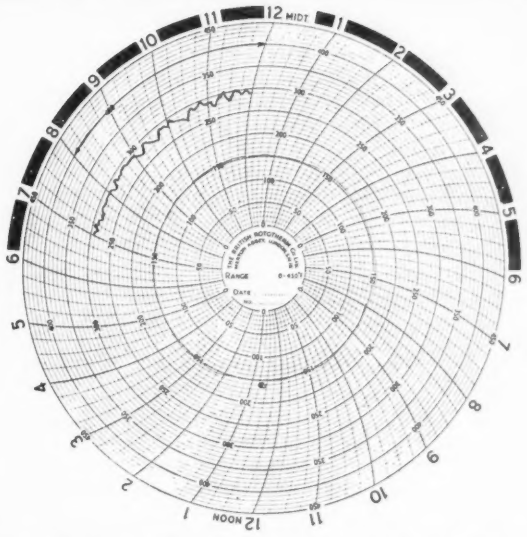


Fig. 39—Chart showing inlet and outlet feed-water temperatures at economizer

From 1st August to 31st October the economizer has been in continuous operation for a further 2200 hr., and the total number of hours in operation since being put into commission is 4290.

There has never been any difficulty in keeping the gill passages clear. The steam blowers are operated once every 8 hr., and the undersides of the gills are air-lanced three or four times each week.

Experience has shown that there is no danger from steam formation in the economizer under relatively abnormal conditions. The maximum recorded outlet-feed temperature, even when there was a considerable increase in the gas temperature at the boiler inlet, is 171·1° C. With a working pressure of 250 lb./sq. in., the corresponding temperature of steam formation being about 207·8° C., a feed-water exit temperature as high as 182·2° C. would still leave a margin of 25·6° C. below steam formation.

Where inlet gas-temperature changes are abnormal, owing to prolonged periods between furnace reversals, the outlet feed-water temperature from the economizer fluctuates only slightly more than normal. Recordings of these conditions are shown in Figs. 36–39. Inlet gas temperatures to boiler and economizer, shown in Figs. 36 and 37, record variation at the boiler inlet from 580° to 680° C. and from 250° to 270° C. at the economizer inlet. The equivalent evaporation during the same period as recorded in Fig. 38 shows a rise and fall of about 6700 lb./hr. The rise and fall in outlet water temperature varies about 11° C., as compared with 5·5° C. under normal gas-temperature conditions. This is shown in Fig. 39. The three sharp drops recorded on the evaporation chart (Fig. 38) indicate the periods when the economizer soot blowers were operated.

When two furnaces are in production, each furnace exhausts separately through each half of the boiler and each half of the economizer. When one furnace only is in production the exhaust gases pass through

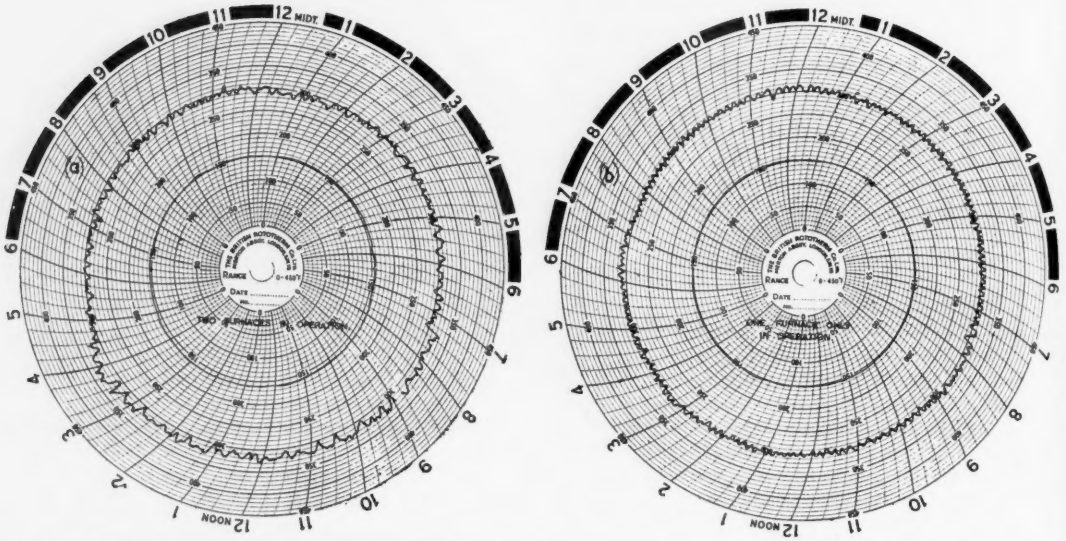


Fig. 40—Chart showing feed-water temperature rise: (*a*) Two furnaces in operation; (*b*) one furnace in operation

the whole of the boiler and economizer. Figure 40 shows recordings of the water-temperature rise through the economizer in both cases.

The following is a summary of the operational conditions relative to the two charts:

Two Furnaces:

Av. inlet gas temperature to boiler (each half)	590° C.
Av. outlet gas temperature from economizer (each half)	220° C.
Av. inlet water temperature to economizer	65·6° C.
Av. outlet water temperature from economizer	151·7° C.
Av. steam temperature	268·3° C.
Av. evaporation	20,000 lb./hr.
Av. increase in evaporation due to economizer (approx. 16%)	2750 lb./hr.

One Furnace:

Av. inlet gas temperature to boiler	560° C.
Av. outlet gas temperature from economizer	170° C.
Av. inlet water temperature to economizer	65·6° C.
Av. outlet water temperature from economizer	151·7° C.
Av. steam temperature	273·9° C.
Av. evaporation	11,800 lb./hr.
Av. increase in evaporation due to economizer (approx. 16%)	1630 lb./hr.

In view of the successful operation of the economizer described, it has been decided to install a second unit on a waste-heat boiler operating in conjunction with an open-hearth melting furnace fired with producer gas.

NEW HAMMER FORGE AT STEEL, PEECH AND TOZER

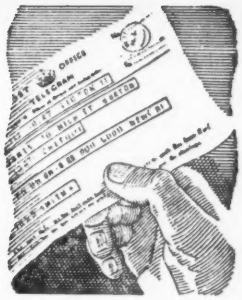
Operations have recently begun at the new hammer forge built by Steel, Peech and Tozer at their Ickles Works and designed to manufacture railway axles.

The new building consists of two bays, one 320 ft. long by 70 ft. wide and the other 240 ft. long by 55 ft. wide. Each bay is served by a 5-ton E.O.T. crane, fitted with a magnetic attachment. The principal items of equipment are a continuous gas-fired furnace, a 7-ton steam-operated hammer, an electrically operated mechanical manipulator, a second furnace and oil tank for heat-treatment purposes, a straightener, and cold-sawing equipment. A 5-ton hammer and two batch-type furnaces are also included for general forging purposes.

The layout of the equipment has been designed on continuous flow principles and an output of over 100 axles per shift can be achieved. The axle blooms are transported in wagons and are unloaded and stacked by an overhead crane. Each bloom is charged as required into the continuous heating furnace, and is gradually heated to 1250° C. On reaching the end of the furnace the bloom is pushed out down a gravity roller rack to the manipulator, which grips the bloom by means of specially designed tongs and, while forging is taking place, rotates it. During this operation a constant stream of water is played on the bloom from a series of jets, to ensure the removal of scale and to give a clean forged surface. When one end of the bloom has been forged the manipulator places it on a turntable, where it is rotated through 180°. The manipulator then grips it by the forged end and returns it to the hammer.

On completion of forging the axle is placed on a tilting gantry and raised to the height of the heat-treatment furnace hearth. It rolls through this furnace by gravity and is heated to about 850° C. On emerging from the furnace it rolls on to a cradle above an oil-bath. If the axle is to be oil-quenched the cradle is submerged for a predetermined time; when the cradle is raised a special ejecting mechanism rolls the axle on to the adjacent turntable. If the axle is to be normalized instead of oil-quenched, it rolls straight over the oil tank to a turntable. After being rotated through 90° the axle moves along to the cooling racks and is then straightened, after which the ends are cold-sawn.

N E W S



ANNOUNCEMENTS AND NEWS OF SCIENCE AND INDUSTRY

THE IRON AND STEEL INSTITUTE

Société Française de Métallurgie

The Société Française de Métallurgie and the Institute of Metals will hold a Joint Spring Meeting in London from Monday to Friday, 26th–30th April, with extension tours in the London area and the provinces lasting until Tuesday, 4th May, 1954.

As the Société covers both ferrous and non-ferrous metallurgy, the Council of the Institute of Metals **invites all members of The Iron and Steel Institute to participate** in this Joint Spring Meeting on the same basis as members of the Institute of Metals.

A programme of papers and/or subjects for discussion on ferrous metallurgy is being arranged in co-operation with The Iron and Steel Institute, and the full programme, with a Reply Form, will be sent to all members of both Institutes resident in Great Britain; others who would like to attend are requested to apply for copies. Members who hope to be present are asked to notify the Secretary of the Institute of Metals as soon as possible; those hoping to take tickets for the Banquet and Dance in the Great Room of Grosvenor House (tickets 35*s*. each) are also asked to advise him as early as possible.

Provisional Programme

Monday, 26th April—Opening ceremony of the meeting, followed by the May Lecture, to be given by Professor L. F. Bates, on the magnetic characteristics of metals.

Tuesday, 27th April—Annual General Meeting of the Institute of Metals, and a non-ferrous scientific session. In the morning there will be a cocktail party, and in the evening a Reception given by Her Majesty's Government, for members and ladies of the Société.

Wednesday, 28th April—Symposium on "*The Control of Quality in the Production of Wrought Non-Ferrous Metals and Alloys*," and discussions on precipitation hardening, creep, and ferrous metallurgy. In the evening a Banquet and Dance will be held.

Thursday, 29th April—Discussion on "*Recovery and Recrystallization*," "*Continuous Casting*," and "*Molybdenum and Molybdenum Alloys and the Arc Melting of Metals*." There will be visits to works and laboratories, and in the evening a Reception given by the French Ambassador.

Friday, 30th April—Visits to works or laboratories outside London, or to Cambridge.

Affiliated Local Societies

The Council has decided that as from 1st January, 1954, Ordinary Members who are also members of an Affiliated Local Society will be entitled to pay the reduced rate of subscription to the Institute of £3 13s. 6d. per annum. Members will be notified of detailed arrangements shortly,

NEWS OF MEMBERS

▶ Mr. B. B. ARGENT has been awarded the degree of B.Met. with 1st Class Honours and a Mappin Medal in metallurgy, at the University of Sheffield.

▶ Mr. W. C. BELL, local director and joint director in charge of research and technical development of Stewarts and Lloyds Ltd., has been awarded the American Iron and Steel Institute Medal for 1953, for a paper on "*Operating and Technical Practices in the European Iron and Steel Industry*," which he delivered in New York on 27th May, 1953.

This is the first time that the medal has been awarded to a person who is not a citizen of the U.S.A.

▶ Dr. G. P. CONTRACTOR has left India for Canada, where he has taken up an appointment with the Falconbridge Nickel Mines Ltd., and is working in the Bureau of Mines Laboratories at Ottawa.

▶ Mr. W. H. CRAWSHAW has returned to the U.K. from Canada, and has taken up an appointment with the Morgan Crucible Co., Ltd.

▶ Mr. D. GILBEY has been awarded his B.Sc. and A.R.S.M. at the Royal School of Mines, and has left the U.K. for the Gold Coast to take up an appointment with Bibiani (1927) Ltd.

▶ Mr. T. W. HAND has become a Consultant to Stein and Atkinson Ltd.

▶ Mr. R. J. HARBORD, has joined John Lysaghts (Scunthorpe) Ltd., as a Student Metallurgist.

▶ Mr. D. JAMIESON is now employed as a Research Fellow with the Ontario Research Foundation, Toronto, Canada.

▶ Mr. W. T. LAVERTON has retired from active management of Robert Hyde and Son Ltd. but will continue as a Director of the Company.

▶ Mr. W. E. MAHIN has left the Armour Research Foundation, Chicago, to become Technical Director of the Cambridge Plant of the Vanadium Corporation of America, Cambridge, Ohio.

▶ Mr. J. MEAKIN has been awarded an Associateship in Metallurgy at the University of Sheffield.

▶ Mr. JAMES MITCHELL, C.B.E., delivered the Harold Wright Memorial Lecture at the Cleveland Scientific and Technical Institution, Middlesbrough, on 12th November, 1953.

▶ Mr. J. G. PARR has left the British Columbia Research Council to take up an appointment as Research Associate in the Department of Mining and Metallurgy of the University of British Columbia.

▶ Mr. R. B. POTTER, Chairman of Simon-Carves Ltd., has joined the Board of Davy and United Engineering Co., Ltd.

▶ Mr. R. TATE has left the Defence Research Board of Canada to take up a post as Metallurgist with Trans-Canada Air Lines, Winnipeg.

▶ Mr. A. V. WIEBEL has left the Tennessee Coal, Iron and Railroad Co., and has been appointed President of the Tennessee Coal and Iron Division of the United States Steel Corporation.

▶ Mr. S. C. WILSDON has retired from active connection with the B.S.A. Co., Ltd., but will continue his association in an advisory capacity with the subsidiary firms, Monochrome Ltd., and Metal and Plastic Compacts Ltd., of which he is a Founder Director.

▶ Mr. N. YARWORTH has left the U.K. and has taken up an appointment with the Metals and Controls Corporation, Attleboro, Mass., U.S.A.

Obituary

Mr. R. FROST, of the Steel Company of Wales Ltd., on 16th October, 1953.

Mr. F. M. PARKIN, founder of F. M. Parkin (Sheffield) Ltd., on 3rd November, 1953, aged 71.

CONTRIBUTORS TO THE JOURNAL

R. McDonald—In charge of the efficient utilization of Works Services at the Dalzell Works of Colvilles Ltd.

Mr. McDonald was born in Kilmarnock, Ayrshire, and received his technical education at Paisley Technical College and at Sothern's Marine College, Glasgow. He served an apprenticeship at MacGregor's Marine Engineering Works, Port Glasgow, and then joined the Merchant Service, holding several appointments as an Engineer. During this time he obtained a 1st Class Board of Trade certificate as a steam engineer. On leaving the Merchant Service he joined the Colvilles Group, and was for a time employed with the Clyde Alloy Steel Co., Ltd. In 1946 he was appointed Boiler Superintendent and Steam Engineer at the Dalzell Works, where he took up his present appointment in 1951. During the last four years Mr. McDonald has been engaged in research on waste-heat recovery from open-hearth steel melting furnaces.

Terkel Rosenqvist—Lecturer in Metallurgy at the Technical University of Norway.

Mr. Rosenqvist was born in 1921, and studied chemistry at the University of Oslo, where he was awarded the degree of "cand. real." From 1944 until 1947 he was employed in various Norwegian electro-metallurgical industries, and was for a short time Lecturer in Metallurgy at the Technical University of Norway. From 1947 to 1952 he was connected with the Institute for the Study of Metals, University of Chicago, first as Instructor and later as Assistant Professor. He then took up his present appointment, where his work has been concerned with magnetic and crystallographic studies on semi-metallic compounds and with thermodynamic investigations on metal sulphides.

R. McDonald

T. Rosenqvist

IRON AND STEEL ENGINEERS GROUP

The **Twenty-Fifth Meeting** of the Iron and Steel Engineers Group will be held at 4 Grosvenor Gardens, London, S.W.1, on **Thursday, 18th March, 1954.** Two papers will be presented for discussion: "*Water Treatment*," by A. J. Lamb; and "*Modern Industrial Steam Generation*," by C. Ungoed. Further details of the programme will be given in a later issue of the *Journal*.

BRITISH IRON AND STEEL RESEARCH ASSOCIATION

21st Blast-Furnace Conference

The 21st Blast-Furnace Conference was held at Ashorne Hill, Leamington Spa, on 13th and 14th October, 1953. The Chairman of the Conference was Mr. G. H. Johnson. During the first session, Major W. R. Brown reviewed the developments in blast-furnace engineering since 1930. The most noticeable change in the furnace itself is in hearth diameter, which in some large units is now from 25 to 29 ft. Crushing, screening, and ore drying and bedding have been introduced. Large electrically operated transfer cars, ore bridge cranes spanning 300 ft. and capable of operating at 800 tons/hr., and air and steam tipping ladles of up to 400 cu. ft. capacity have improved methods of handling. During discussion, hot blast valves, manufacture of large bells, conveying systems, stoves and slag notch stoppers were considered.

Dr. A. T. Green introduced the second session by describing developments in blast-furnace refractories. He compared early tests on carbon monoxide attack and improved methods of investigation used today. The deterioration of linings by this attack still occurred due to the inherent iron content of the clay from which standard refractories are made. In discussion, reference was made to the effect of the rate of blowing-in on the life of refractories, and it was felt that the method of blowing-in also affected this problem. In regard to scaffolds, the phenomenon was considered to have a chemical origin coincident with certain conditions existing in the furnace.

The stages of development which had led to the present-day degree of ore preparation were reviewed by Dr. T. P. Colclough in the third session. Early studies concerned with the relationship between the resistance to gas flow and particle size of raw materials emphasized the need for ore crushing to obtain uniformity of size for maximum efficiency in the furnace. Uniformity of composition was now achieved by ore bedding and sintering. These preparations had led to more even driving and stock descent, together with improved indirect reduction of the burden with lower throughput times. The ultimate aim was complete preparation of materials in order to increase the efficiency of the furnace process. In discussion, it was agreed that beneficiation of the burden had reduced slips and uneven working; preparation of coke was also an important factor. Large quantities of alkali oxides were included in some furnace burdens, but it was doubtful whether any form of treatment would completely eliminate these alkalis. Reference was made to the use of black band ironstone, and although the cost of mining these seams was high and the volatile matter was from 40–45%, the use of this material in the blast-furnace had not been overlooked.

At the fourth session, a review of research in iron-making was presented by Dr. H. L. Saunders. After early fundamental experiments on reaction rates and equilibria, the Industrial Research Council was formed, and in 1930 the first full-scale blast-furnace trials were

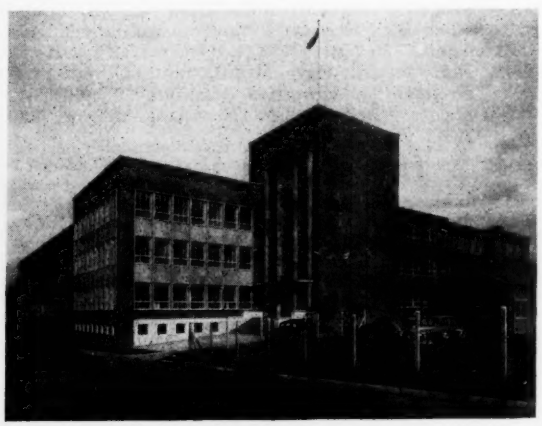
carried out in this country. With the formation of B.I.S.R.A., co-operative research had increased, and further basic theories of blast-furnace reactions were established. Full-scale field tests concerned with distribution, gas transit times, furnace exploration, pelletizing, sintering, and desulphurization were now an integral part of the current research programme.

At the final session, Mr. D. W. E. Lloyd outlined the effect of developments in blast-furnace operation on the working conditions of the operator. Reference was made to the difficulties that operators had to contend with under conditions existing in 1902. In recent years research and development had removed some of these obstacles, but only by the assimilation of the basic theories, implemented by practical experience, could the younger operator succeed. Tribute was paid to the work of many operators and investigators who had been closely connected with ironmaking, and in particular to Sir William Larke, Mr. E. C. Evans, Mr. C. A. J. Behrendt, Mr. T. Burnicle, and Dr. M. A. Vernon, all of whom were present.

Opening of Sheffield Laboratories

An important occasion in the history of the Association was marked on Thursday, 19th November, when the new laboratories at Sheffield were officially opened by H.R.H. The Duke of Edinburgh.

Since its formation in 1945, the policy of the Association has been to place its laboratories in those parts of the country where particular branches of the industry can best be served. Sheffield was chosen as an appropriate centre for research on the making, working, and metallurgy of steel. The modern buildings constructed, on the old site of one of the longest-established steel firms in the city, were completed in three years, and are a great tribute to those who planned and built them. Comprising one of the finest research establishments in the world, they contain much of the equipment of a steelworks in miniature, including pilot machinery for melting, rolling, drawing, and forging. The Duke was conducted round the laboratories in a party which included his private secretary, Lieutenant Commander J. M. A. Parker, M.V.O., R.N., the Lord Mayor of Sheffield, the Lord Lieutenant of the West Riding the Earl of Scarborough, and the Chief Constable and Town Clerk of Sheffield. During his tour he was able to see such equipment as a 200-ton forging press; a ½-ton electric arc furnace; a 4-high cold rolling mill with a maximum speed of 1750 ft./min.; a 2-hole, straight-line wire drawing machine; and a 55-lb. vacuum melting induction furnace.



After the tour, a number of distinguished visitors were present at the opening ceremony, at which Lord Dudley Gordon, the President of B.I.S.R.A. introduced His Royal Highness, who congratulated the steel industry on the way in which it has tackled the problem of improving output. "*World industrial competition is bound to get keener in the years ahead*," he said, "*Therefore it is comforting to know our steel industry still has the pioneering spirit and the necessary laboratory backing to keep it well in the fight for world markets.*" After his speech, His Royal Highness was presented with a gold-handled pocket knife by Captain H. Leighton Davies, Chairman of B.I.S.R.A. A number of the staff of the Association were presented to the Duke, including the Director, Sir Charles Goodeve, and the Secretary, Mr. N. A. Everett.

The illustration shows the new main block of the group of buildings, which covers 30,000 sq. ft. of floor area. The other two new buildings are a metal-working shop (10,000 sq. ft.) and a melting shop (4000 sq. ft.). Some older buildings, including a cutlery laboratory, are also in use, and were included in the Royal visit.

AFFILIATED LOCAL SOCIETIES

Lincolnshire Iron and Steel Institute

The list of Officers for the Session 1953–54 is as follows:

President
W. L. JAMES, J.P.

Vice-Presidents

S. G. DAVIES	A. H. NORRIS
G. D. ELLIOT	L. REEVE
J. L. GASKELL	J. D. TOWNSEND
T. JONES	N. H. TURNER
I. M. KEMP	G. W. WELLS

W. T. WILSON

Hon. Secretary
C. H. WARBURTON

Hon. Treasurer
G. P. ELSON

Council

D. BRUCE-GARDNER	J. McLAUCHLAN
A. BRIDGE	W. JACKSON
J. DODD	J. A. PEACOCK
W. GEARY	T. E. SHAW

A. C. WATKISS

NEWS OF SCIENCE AND INDUSTRY

International Union of Crystallography

The 3rd General Assembly and International Congress of the International Union of Crystallography will be held in Paris from 21st to 28th July, 1954. Papers on all aspects of crystallographic research will be presented, and there will also be an exhibition of crystallographic apparatus and books. After the Congress, two specialized Symposia will be held on "*The Location and Function of Hydrogen*" and "*The Mechanism of Phase Transitions in Crystals.*" Visits will also be made to places of mineralogical interest. Full details of the Congress are given in the First Circular, copies of which are obtainable from the General Secretary of the Union, Mr. R. C. Evans, Crystallographic Laboratory, Cavendish Laboratory, Cambridge.

Staff School Open Awards

To encourage a wider study of technical and administrative problems in the iron and steel wire industry, the Staff School of Frederick Smith and Co. will make awards totalling 300 guineas for the best papers on the subject. The competition will be divided into a technical

and an administrative section, and separate awards will be made in each group. Entry forms may be obtained from the Secretary, The Staff School, Caledonia Works, Halifax, and must be completed and returned by 28th February, 1954. Closing date for receipt of papers submitted for the competition is 31st May, 1954.

British Standards Institution

Sir Roger Duncalfe, Chairman of British Glues and Chemicals, has been elected President of the British Standards Institution, in succession to Viscount Waverley.

Kelvin Medal

The Kelvin Gold Medal for 1953 has been awarded to Dr. Chalmers Jack Mackenzie, C.M.G., Ll.D., F.R.S., M.C., of Canada.

Suspension of Restrictions on the Use of Nickel

The Council of the Organization for European Economic Co-operation has suspended the common list of restrictions on the use of nickel, nickel alloys, and nickel-plating, and the application of measures limiting the use of nickel in case-hardening and constructional steels.

Iron and Steel Foundries Regulations, 1953

The Minister of Labour and National Service, Sir Walter Monckton, Q.C., has made Regulations under the Factories Acts which make provision for the safety, health, and welfare of workers employed in iron and steel foundries. They contain requirements as to gangways, suppression of dust and fumes, protective equipment, bathing facilities, clothing accommodation, and the arrangements and storage of foundry equipment, tools, etc., and will come into operation on 1st January, 1954, with the exception of the requirements relating to the suppression of dust and fumes, bathing facilities, and clothing accommodation, which operate from 1st January, 1956. These regulations have now been published and are obtainable from H.M.S.O. or through any bookseller, price 4*d*.

CORRIGENDUM

Activities of Constituents of Iron and Steelmaking Slags—Part III

The following correction should be made to the paper by E. T. Turkdogan and J. Pearson (*J. Iron Steel Inst.*, 1953, vol. 175, Dec., pp. 398–401):

In Fig. 2, p. 400, the crosses represent 1660 $\pm$ 10° C.

DIARY

5th Jan.—SWANSEA AND DISTRICT METALLURGICAL SOCIETY (Joint meeting with The Iron and Steel Institute)—Paper on Slags, by W. R. Maddocks—Central Library, Swansea, 7.0 P.M.

7th Jan.—LEEDS METALLURGICAL SOCIETY—"*Some Applications of Spheroidal Graphite Cast Iron*," by A. B. Everest—Chemistry Department, The University, Leeds 2, 7.15 P.M.

9th Jan.—INSTITUTE OF BRITISH FOUNDRYMEN (Newcastle Branch)—"*Residual Stresses in Castings*," by R. N. Parkins—Neville Hall, Westgate Road Newcastle-on-Tyne, 6.0 P.M.

11th Jan.—CLEVELAND INSTITUTION OF ENGINEERS—"*Flame Radiation and O.H. Productivity*," by M. W. Thring—Cleveland Scientific and Technical Institution, Corporation Road, Middlesbrough, 6.30 P.M.

11th Jan.—INSTITUTION OF PRODUCTION ENGINEERS (Sheffield Section)—"*Extrusion of Metals*," by J. T. Lewis—Grand Hotel, Sheffield, 6.30 P.M.

12th Jan.—SHEFFIELD METALLURGICAL ASSOCIATION—"*Silicon Carbide Refractories*," by G. Brooks—B.I.S.R.A., Hoyle Street, Sheffield, 7.30 P.M.

12th Jan.—NORTH EAST METALLURGICAL SOCIETY—Metallurgical Brains Trust—Cleveland Scientific and Technical Institution, Corporation Road, Middlesbrough, 7.15 P.M.

14th Jan.—STAFFORDSHIRE IRON AND STEEL INSTITUTE—"*Hardness*," by H. O'Neill—Victoria Hotel, Wolverhampton, 7.30 P.M.

14th Jan.—LIVERPOOL METALLURGICAL SOCIETY—Discussion on "*The Corrosion and Preservation of Metals*" — Liverpool Engineering Society, The Temple, Dale Street, Liverpool, 7.0 P.M.

15th Jan.—NORTH EAST COAST INSTITUTION OF ENGINEERS AND SHIPBUILDERS—"*Metallurgical Aspects of High-Temperature Steam and Gas Turbine Plants*," by J. M. Robertson—Mining Institute, Neville Hall, Newcastle-on-Tyne, 6.15 P.M.

18th Jan.—CLEVELAND INSTITUTION OF ENGINEERS—"*Engineering and Operational Aspects of New Rolling Mill Plant at Normanby Park Steelworks*," by K. S. Peacock and A. H. Norris—Cleveland Scientific and Technical Institution, Corporation Road, Middlesbrough, 6.30 P.M.

18th Jan.—SHEFFIELD SOCIETY OF ENGINEERS AND METALLURGISTS—Presidential Address—University Building, St. George's Square, Sheffield, 7.30 P.M.

19th Jan.—LINCOLNSHIRE IRON AND STEEL INSTITUTE—"*Some Aspects of the Basic Bessemer Process*," by J. Glen—Wortley Hotel, Scunthorpe, 7.30 P.M.

20th Jan.—SOCIETY OF INSTRUMENT TECHNOLOGY (South Yorkshire Section)—"*Temperature Measurement at the N.P.L.*," by J. Hall—University Buildings, St. George's Square, Sheffield, 7.0 P.M.

20th Jan.—INSTITUTE OF FUEL (Yorkshire Section)—"*Hot Blast Cupola Practice*," by W. J. Driscoll—The University, Leeds, 6.30 P.M.

20th Jan.—NEWPORT AND DISTRICT METALLURGICAL SOCIETY—"*Recent Developments in Furnace Design*," by R. J. Sarjant—Whitehead Institute, Cardiff Road, Newport, 7.0 P.M.

20th Jan.—ROYAL INSTITUTE OF CHEMISTRY (London Section)—"*The Manufacture of Iron and Steel*," by D. J. O. Brandt—King's College Chemistry Lecture Theatre, Strand, London, W.C.2, 6.0 P.M.

20th Jan.—SOCIETY OF CHEMICAL INDUSTRY (Corrosion Group)—"*Metallurgical Aspects of Dry Corrosion*," by L. B. Pfeil—Chemical Society, Burlington House, Piccadilly, London, W.1, 6.30 P.M.

21st Jan.—SOCIETY OF CHEMICAL INDUSTRY (Corrosion Group)—Exhibition and Conversazione—Battersea Polytechnic, Battersea Park Road, London, S.W.11, 6.30 P.M.

22nd Jan.—STAFFORDSHIRE IRON AND STEEL INSTITUTE (Associates' Section)—Film show on "*Iron and Steelmaking Processes*"—Stewarts and Lloyds Ltd., Bilston, 7.30 P.M.

22nd Jan.—NORTH EAST METALLURGICAL SOCIETY—"*Evolution in Extraction Metallurgy*," by C. W. Dannatt—King's College, Newcastle-on-Tyne, 7.15 P.M.

TRANSLATION SERVICE

(The previous announcement was made in the December, 1953, issue of the *Journal*, p. 424).

TRANSLATIONS IN COURSE OF PREPARATION

(German). W. SCHEURER: "Influence of the Furnace Atmosphere on the Surface Finish of Round Ingots and Tubes." (*Stahl und Eisen*, 1952, vol. 72, July 31, pp. 935–941).

(German). F. KÖSTERS: "Quenching of Basic Bessemer Steel from the Rolling Temperature in Full-Scale Operation." (*Stahl und Eisen*, 1953, vol. 73, Oct. 8, pp. 1342–1348).

ABSTRACTS AND BOOK NOTICES

IRON AND STEEL MANUFACTURE AND RELATED SUBJECTS

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ABBREVIATIONS AND LIST OF PERIODICALS EXAMINED BY THE ABSTRACTING SERVICE

Abhandlungen der **Braunschweig**ischen **wiss**enschaftlichen **Ges**ellschaft (Brunswick)
Acciaio Inossidabile (Milan)
Acero y Energia (Barcelona)
Acid Open Hearth Research **Assoc**iation, **Bull**etin (Pittsburgh)
Aciers Fins et **Spec**iaux **Fran**çais (Paris)
Acta Crystallographica (London)
Acta Metallurgica (Toronto)
Acta Polytechnica (Stockholm)
Acta Technica (Budapest)
Advancement of **Sc**ience (London)
Advances in **Phys**ics (London)
Aeroplane (London)
Aircraft Engineering (London)
Aircraft Production (London)
Alloy Castings **Bull**etin (New York)
Alloy Metals Review (Widnes)
Alluminio (Milan)
Aluminium (Düsseldorf)
Aluminium Development **Assoc**iation, **Information Bull**etin (London)
American Electroplaters' **Soc**iety, **Res**earch **Rep**orts (Jenkintown, Pa.)
American Foundryman (Chicago)
American Foundrymen's **Soc**iety, **Pre**print (Chicago)
American Institute of **Min**ing and **Met**allurgical **Eng**ineers (New York)
Blast Furnace and **Raw Mat**erials **Com**mittee
Proceedings **Electric Furn**ace **Steel Conf**erence
Proceedings **Nat**ional **Open-Hearth Com**mittee
Proceedings **Symposia Series**
American Iron and **Steel Inst**itute (New York)
Annual Statistical **Rep**ort
Contributions to the **Met**allurgy of **Steel**
Steel Products **Man**ual
American Journal of **Phys**ics (New York)
American Journal of **Sc**ience (New Haven, Conn.)
American Society for **Metals, Preprint** (Cleveland, Ohio)
American Society for **Test**ing **Mat**erials (Philadelphia)
Preprint
Special Technical Publication
Anais da **Acad**emia **Brasil**eira de **Cienc**ias (Rio de Janeiro)
Anais da **Associação Quím**ica do **Brasil** (Rio de Janeiro)
Anales da la **Asoc**iacion **Quím**ica **Argentina** (Buenos Aires)
Anales de la Real Sociedad Española de **Fis**ica y **Quím**ica (Madrid)
Anales de **Mec**anica y **Electr**icidad (Madrid)
Analyst (London)
Analytica Chimica **Acta** (New York and Amsterdam)
Analytical Chemistry (Washington)
Annales des Mines (Paris)
Annales de la **Société Scientifique** de **Bruxelles** (Brussels)
Annual Proceedings of the **Sheet** and **Strip Metal Users' Tech**nical **Assoc**iation (London)
Annual Report of the **Smithsonian Inst**itution (Washington)
Anvil (Sheffield)
Applied Mechanics **Rev**iews (New York)
Applied Research **Lab**oratories, **Rep**orts (Glendale, Calif.)
Applied Scientific Research (The Hague)
Archiv für das **Eisenhüttenwesen** (Düsseldorf)
Arkiv för **Fysik** (Stockholm)
Arkiv för **Kemi** (Stockholm)
Arkiv för **Min**eralogi och **Geo**logi (Stockholm)
Arts et Manufacturers (Paris)
Atomics (London)
Atti della **Acc**ademia **Naz**ionale dei **Lincei. Rend**iconti della **Classe** di **Sc**ienze **Fis**iche, **Mat**ematiche e **Nat**urali (Rome)
Australasian Engineer (Sydney)
Australasian Plating and **Fin**ishing (Melbourne)
Australian Foundry Trade Journal (Sydney)
Australian Journal of **Applied Sc**ience (Melbourne)
Australian Journal of **Chem**istry (Melbourne)
Australian Journal of **Phys**ics (Melbourne)
Australian Machinery (Sydney)
Automobile Engineer (London)
Avtogennoe Delo (Moscow)

B.H.P. Review (Melbourne)
Ball Bearing Journal (Luton)
Battelle Technical **Rev**iew (Columbus, Ohio)
Beama Journal (London)
Bell Laboratories **Record** (New York)
Bell System Technical **Journal** (New York)
Bell Telephone Laboratories **Tech**nical **Pub**lication (New York)
Bell Telephone Magazine (New York)
Berg- und **hüttenmännische Monatsh**efte (Vienna)

LIST OF PERIODICALS

Bibliographical Bulletin of Welding (Paris)
Blad for Bergshandteringens Vänner (Stockholm)
Blast Furnace and Steel Plant (Pittsburgh)
Boletim da Associação Brasileira de Metais (São Paulo)
Boletim da Associação Química do Brasil (Rio de Janeiro)
Boletim da Sociedade Geológica de Portugal (Oporto)
Boletim do INT (Rio de Janeiro)
Boletin del Instituto Geológico y Minero de España (Madrid)
Boletin Minero e Industrial (Bilbao)
Brennstoff–Wärme–Kraft (Dusseldorf)
British Cast Iron Research Association, Journal of Research and Development (Birmingham)
British Coal Utilisation Research Association, Monthly Bulletin (London)
British Coke Research Association, Technical Papers (London)
British Dental Journal (London)
British Electrical and Allied Industries Research Association, Reports (London)
British Engineering (London)
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British Journal of Applied Physics (London)
British Steelmaker (London)
British Welding Journal (London)
Brown-Boveri Review (Baden)
Bulletin of the American Ceramic Society (Columbus, O.)
Bulletin, American Society for Testing Materials (Philadelphia)
Bulletin of the British Scientific Instrument Research Association (London)
Bulletin, British Steel Founders' Association (Sheffield)
Bulletin de Cercle d'Etudes des Métaux (St. Etienne)
Bulletin and Foundry Abstracts of the British Cast Iron Research Association (Birmingham)
Bulletin of the Geological Institute of the Upsala University (Upsala)
Bulletin of the Institute of Metal Finishing (London)
Bulletin of the Institution of Metallurgists (London)
Bulletin of the Institution of Mining and Metallurgy (London)
Bulletin of Ohio State University Engineering Experiment Station (Columbus, O.)
Bulletin of the School of Mines and Metallurgy, University of Missouri (Minneapolis)
Bulletin des Sociétés Chimiques Belges (Brussels)
Bulletin of the University of Wisconsin, Engineering Experiment Station Series

Canadian Journal of Chemistry (Ottawa)
Canadian Journal of Physics (Ottawa)
Canadian Journal of Technology (Ottawa)
Canadian Metals (Toronto)
Canadian Mining Journal (Quebec)
Canadian Mining and Metallurgical Bulletin (Montreal)
Calore (Milan)
Centre de Documentation Sidérurgique, Circulaires d'Informations Techniques (Paris)
Ceramics (Leighton Buzzard)
Chaleur et Industrie (Paris)
Chemical Age (London)
Chemical Engineering (New York)
Chemical Engineering and Mining Review (Melbourne)
Chemical and Engineering News (Washington)
Chemical Engineering Progess (New York)
Chemické Listy (Prague)
Chemisch Weekblad (Amsterdam)
Chemist-Analyst (Phillipsburg, N.J.)
Chemistry and Industry (London)
Chimica e Industria (Milan)
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Circular of the National Bureau of Standards (Washington)
Circular of Ohio State University Engineering Experiment Station (Columbus)
Claycraft (London)
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Colorado School of Mines, Quarterly (Golden, Colorado)
Commonwealth Engineer (Melbourne)
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences (Paris)
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Corrosion (Houston, Texas)
Costruzioni Metalliche (Milan)
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Demag News (Duisburg)
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E.S.C. News (Sheffield)
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Electroplating (London)
Elektrotechnik und Maschinenbau (Vienna)
Elektrotechniski Vestnik (Ljubljana, Yugoslavia)
Elektrowärme Technik (Mindelheim)
Elliott Journal (London)
Endeavour (London)
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Engineer (London)
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Engineering (London)
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Engineering and Mining Journal (New York)
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Experimentia (Basle)

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Fonderia Italiana (Milan)
Fonderie (Paris)
Forschung auf dem Gebiete des Ingenieurwesens (Düsseldorf)
Foundry (Cleveland)
Foundry Trade Journal (London)
Freyn Design (Chicago)
Fuel (London)
Fuel Economy Review (London)
Fuel Society Journal (Sheffield)

G.E.C. Journal (London)
Galvano (Paris)
Gas Research Board Communications (Beckenham)
Gas Times (Watford)
Gas World (London)
Gazzetta Chimica Italiana (Rome)
Génie Civil (Paris)
Geologiska Föreningens Förhandlingar (Stockholm)
Giesserei (Düsseldorf)
Gjuteriet (Stockholm)
Glückauf (Essen)

Hutnické Listy (Prague)
Hutnik (Prague)
Hutnik (Poland)

IVA Ingeniörs Vetenskaps Akademien (Stockholm)
Illinois University Engineering Experiment Station (Urbana)
Circular
Bulletin
Indian Journal of Physics (Calcutta)
Industria y Química (Buenos Aires)
Industrial Chemist (London)
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Institut pour l'Encouragement de la Recherche Scientifique, Comptes Rendus de Recherches (Brussels)

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Instituto de la Soldadura, Publicacíon (Madrid)
Instituto Nacional del Carbon Boletin Informativo (Oviedo)
Instituto Nacional de Tecnologia Boletin (Rio de Janeiro)
Instrument Engineer (Luton)
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Iron Age (New York)
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Journal of the American Water Works Association (New York)
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Journal of Applied Chemistry (London)
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Journal of the Birmingham Metallurgical Society (Birmingham)
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Journal of Chemical Physics (New York)
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Journal de Chimie Physique (Paris)
Journal of the Council for Scientific and Industrial Research (Melbourne)
Journal of Dental Research (Baltimore)
Journal of the Electrodepositors' Technical Society (London)
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Journal of the Franklin Institute (Lancaster, Pa.)
Journal of the Indian Chemical Society (Calcutta)
Journal of the Institute of Australian Foundrymen (Melbourne)
Journal of the Institute of Fuel (London)
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Journal of the Institution of Automotive and Aeronautical Engineers (Melbourne)
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Journal of the Institution of Engineers, Australia (Sydney)
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Journal, Institution of Mechanical Engineers (London)
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Journal of Mechanical Laboratory (Tokyo)
Journal of the Mechanics and Physics of Solids (London)
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Journal de Physique et le Radium (Paris)
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Journal of the Royal Artillery (London)
Journal of the Royal Institute of British Architects (London)
Journal of the Royal Microscopical Society (London)
Journal of the Royal Society of Arts (London)
Journal of the Royal Statistical Society (London)
Journal of the Royal Technical College (Glasgow)
Journal of Scientific Instruments (London)
Journal of Scientific and Industrial Research (New Delhi)
Journal of the Scientific Research Institute (Tokyo)
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Journal of the South African Institution of Mechanical Engineers (Johannesburg)
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Kyoto University, Engineering Research Institute, Technical Reports (Kyoto)

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Memoirs of the Faculty of Science, Kyuoyu University (Hukuoka, Japan)
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Metalurgia y Electricidad (Madrid)
Metallurgia Italiana (Milan)
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Mining Journal (London)
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Modern Metals (Chicago)
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National Physical Laboratory, Reports (Teddington)
Nature (London)
New Zealand Engineering (Wellington)
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Nickel Bulletin (London)
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Operational Research Quarterly (London)

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Osaka University, Faculty of **Engineering Technology Reports** (Osaka)
Ossature Métallique (Brussels)
Österreichischer Maschinenmarkt mit **Elektrowirtschaft** (Vienna)
Overseas Engineer (London)

Peintures, Pigments, Vernis (Paris)
Philippine Geologist (Manila)
Philips Research Reports (Eindhoven)
Philips Technical Review (Amsterdam)
Philosophical Magazine (London)
Philosophical Transactions of the **Royal Society** (London)
Physical Review (New York)
Planseeberichte für Pulvermetallurgie (Reutte, Tyrol)
Plating (Jenkintown, Pa.)
Powder Metallurgy Bulletin (Yonkers N.Y.)
Post Office Electrical Engineers' Journal (Epsom)
Prace Instytutow Ministerstwa Hutnictwa (Poland)
Pratique du Soudage (Brussels)
Precision Metal Molding (Cleveland)
Proceedings, American Gas Association (New York)
Proceedings of the **American Society** for **Testing Materials** (Philadelphia)
Proceedings of the...**Annual Convention** of the **American Electroplaters' Society** (Jenkintown, Pa.)
Proceedings, Australasian Institute of **Mining** and **Metallurgy** (Melbourne)
Proceedings of the **Australian Institute** of **Metals** (Melbourne)
Proceedings of the **Cambridge Philosophical Society** (London)
Proceedings, Chemical Engineering Group (London)
Proceedings, Diesel Engine Users' Association (London)
Proceedings of the **Durham Philosophical Society** (Durham)
Proceedings of the **Ebbw Vale Metallurgical Society** (Ebbw Vale)
Proceedings of the **Indian Academy** of **Sciences** (Bangalore)
Proceedings of the **Indiana Academy** of **Sciences** (Greencastle, Ind.)
Proceedings of the **Institute** of **Australian Foundrymen** (Melbourne)
Proceedings of the **Institute** of **British Foundrymen** (Manchester)
Proceedings of the **Institution** of **Electrical Engineers** (London)
Proceedings, Institution of **Mechanical Engineers** (London)
Proceedings of the **Institution** of **Mechanical Engineers, Automobile Division** (London)
Proceedings of the **Japan Academy** (Tokyo)
Proceedings of the **Lincolnshire Iron** and **Steel Institute** (Scunthorpe)
Proceedings, Metal Powder Association (New York)
Proceedings, Natural Gas Department of the **American Gas Association** (New York)
Proceedings of the **Nova Scotian Institute** of **Science** (Halifax)
Proceedings of the **Physical Society** (London)
Proceedings of the **Royal Canadian Institute** (Toronto)
Proceedings of the **Royal Institution** of Great Britain (London)
Proceedings of the **Royal Society** (London)
Proceedings of the **Royal Society** of **Edinburgh** (Edinburgh)
Proceedings of the **Society** of **Experimental Stress Analysis** (Cambridge, Mass.)
Proceedings of the **South Wales Institute** of **Engineers** (Cardiff)
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Product Engineering (New York)
Product Finishing (London)
Products Finishing (Cincinnati)
Pro-Metal (Berne)
Przeglad Odlewnictwa (Cracow)
Przeglad Techniczny (Warsaw and Lodz)
Publications de l'**Association** des **Ingénieurs** de la **Faculté Polytechnique** de **Mons** (Mons)
Publications de l'**Institut** de **Recherches** de la **Sidérurgie** (St. Germain-en-Laye)
Purdue University, Engineering Experimental Department (Lafayette, Ind.)
Engineering Extension Series
Engineering Research Series

Quarterly Journal of the **Geological, Mining**, and **Metallurgical Society** of **India** (Calcutta)
Quarterly Journal of the **Geological Society** (London)
Quarterly Journal of **Mechanics** and **Applied Mathematics** (Oxford)
Queensland Government Mining Journal (Brisbane)

Radex Rundschau (Radenthein)
Railway Gazette (London)
Railway Steel Topics (Sheffield)
Recherche Aéronautique (Paris)
Records of the **Geological Survey** of **India** (Calcutta)
Recueil des **Travaux Chimiques** des **Pays-Bas** (The Hague)
Refractories Journal (London)
Regional Technical Meetings of the **American Iron** and **Steel Institute** (New York)
Reports of the **Scientific Research Institute** (Tokyo)
Research (London)
Research Association of **British Paint, Colour** and **Varnish Manufacturers' Review** (Teddington)
Review of **Scientific Instruments** (New York)
Reviews of **Modern Physics** (New York)
Revista de Ciencia Aplicada (Madrid)
Revista de Química Industrial (Rio de Janeiro)
Revue de l'**Aluminium** (Paris)
Revue de la **Faculté** des **Sciences** de l'**Université** d'**Istanbul**
Revue Générale de Mécanique (Paris)
Revue de l'**Industrie Minérale** (St. Etienne)
Revue de **Métallurgie** (Paris)
Revue des **Produits Chimiques** (Paris)
Revue de la **Soudure** (Lastijdschrift) (Brussels)
Revue du **Nickel** (Paris)
Revue Technique Luxembourgeoise (Luxembourg)
Revue Universelle des **Mines** (Liège)
Rheology Bulletin (New York)
Ricerca Scientifica (Rome)
Roll'schen Eisenwerke A.G. (Gerlafingen, Switzerland)
Mitteilungen
Werkzeitung
Royal Australian Chemical Institute (Melbourne)
Journal and **Proceedings**
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Schweissen und Schneiden (Brunswick)
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Schweizer Archiv für **Wissenschaft** und **Technik** (Solothurn, Switzerland)
Science (Washington)
Science Abstracts (London)
Science and Engineering (Calcutta)
Science Reports of the **Tôhoku University** (Sendai, Japan)
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Scientific Proceedings of the **Royal Dublin Society**
Sheet Metal Industries (London)
Shipbuilder (Newcastle-on-Tyne)
Silicates Industriels (Brussels)
Slévárenstvi (Prague)
Société Royal Belge des **Ingenieurs** et des Industriels (Brussels)
Bulletin Technique
Mémoires
Spectrographic News Letter (Glendale, Calif.)
Stahl und Eisen (Düsseldorf)
Stanki i Instrument (Moscow)
Statens Provningsanstalt (Stockholm)
Berättelse
Meddelande
Steam Engineer (London)
Steel (Cleveland, Ohio)
Steel Processing (Pittsburgh)
Strojirenstvi (Prague)
Structural Engineer (London)
Suiyokwai-Shi, Transactions of the **Mining** and **Metallurgical Alumni Association** (Japan)
Sulzer Technical Review (Winterthur)
Sumitomo Metals (Osaka)
Sveriges Geologiska Undersökning, Årsbok (Stockholm)
Svetsaren (Gothenburg)
Swansea and District **Metallurgical Society, Advance Copies** (Gorseinon)

Technik (Berlin)
Technique et **Humanisme** (Liège)
Technique et **Science Aéronautiques** (Paris)
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Technische Mitteilungen (Rheinhausen)
Tecnicale Industria (Buenos Aires)
Tecnica Metalúrgica (Barcelona)
Teknisk Tidskrift (Stockholm)
Teknisk Ukeblad (Oslo)
Tetsu-to-Hagane (Tokyo)
Tidsskrift for **Kjemi, Bergvesen** og **Metallurgi** (Oslo)
Times Review of **Industry** (London)
Tin and its Uses (Greenford)
Tisco Review (Calcutta)
Tokyo University, Journal of the **Faculty** of **Engineering** (Tokyo)
Transactions of the **American Foundrymen's Society** (Chicago)

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Transactions of the Canadian Institute of Mining and Metallurgy (Montreal)
Transactions of the Danish Academy of Technical Sciences (Copenhagen)
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Transactions of the Indian Institute of Metals (New Delhi)
Transactions of the Institute of Marine Engineers (London)
Transactions of the Institute of Welding (London)
Transactions of the Institution of Chemical Engineers (London)
Transactions of the Institution of Engineers and Shipbuilders in Scotland (Glasgow)
Transactions, Institution of Gas Engineers (London)
Transactions of the Institution of Mining Engineers (London)
Transactions of the Institution of Mining and Metallurgy (London)
Transactions of the Institution of Naval Architects (London)
Transactions of the Liverpool Engineering Society (Liverpool)
Transactions, Manchester Association of Engineers (Manchester)
Transactions of the Mining, Geological and Metallurgical Institute of India (Calcutta)
Transactions of the Newcomen Society (London)
Transactions of the North East Coast Institution of Engineers and Shipbuilders (Newcastle-on-Tyne)
Transactions of the Royal Canadian Institute (Toronto)
Transactions of the Royal Society of Canada (Ottawa)
Transactions of the Society of Automotive Engineers (New York)
Transactions of the Society of Instrument Technology (London)
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United Effort (Pittsburgh)
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Bulletin
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Universität für technische Wissenschaften, Fakultät für Berg-, Hütten-, und Forstwesen. Mitteilungen der Berg- und Hüttenmännischen Abteilung (Sopron)
Usco Magazine (Pretoria)
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Waseda University, Report of the Casting Research Laboratory (Tokyo)
Welder (Waltham Cross)
Welding Journal (New York)
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Yearbook of the American Iron and Steel Institute (New York)
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Yearly Proceedings of the Association of Iron and Steel Engineers (Pittsburgh)

Zeitschrift für Erzbergbau und Metallhüttenwesen (Stuttgart)
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ABSTRACTS

MINERAL RESOURCES

Ore. F. G. Percival. (*Lithgow J.*, 1953, **1,** (7), 7–2). An historical survey of British iron ore resources and supplies is followed by an outline of the present-day world supply position. Iron ores are grouped according to modes of origin and occurrence, and figures of reserves are quoted.—E. C.

Where Is the Iron Ore Coming From? H. S. Harrison. (*Blast Furn. Steel Plant*, 1953, **41,** July, 751–754, 792). The probable sources of iron ore for the American steel industry in the future are discussed. The author concludes that Canada and Venezuela will be the primary sources of high-grade ore. The concentrated and agglomerated low-grade home ores will form the major part of the blast-furnace burdens.—B. G. B.

Iron Ore Supply: A New Appraisal of the Outlook. H. S. Harrison. (*Eng. Min. J.*, 1953, **154,** June, 80–83). Estimates are given of U.S. steel output, iron ore requirements, and ore sources for the next 25 years. By 1980, ingot capacity may rise to 150 million (short) tons, requiring 157 million (short) tons of ore, per annum. In view of the depletion of the high-grade Minnesota ore, this total will have to be met by great expansion in the use of concentrates and imported ores.—K. E. J.

The Rôle of Geologists in the Development of the Labrador-Quebec Iron Ore Districts. J. K. Gustafson and A. E. Moss. (*Canad. Min. J.*, 1953, **74,** June, 61–68). The development of the Labrador-Quebec iron deposits which include 400,000,000 tons of high grade ore already discovered has necessitated a vast geological effort. A description is given of this work.—A. G.

Geology of the Country Bordering the Southern Section of Quebec North Shore and Labrador Railway. P. E. Grenier. (*Canad. Min. J.*, 1953, **74,** May, 76–81). Reported mineral occurrences and the economic mineral possibilities of the area are briefly outlined. Several titaniferous magnetite deposits have been reported and magnetite sand deposits at the mouth of the Moisie river are worthy of note.—A. G.

Quebec Annual Review. J. C. Browning. (*Canad. Min. J.*, 1953, **74,** Feb., 101–108). The discovery of immense medium-grade iron ore deposits near Ungava Bay was made in 1952. These can be easily mined but a method of concentration at the site has to be developed. Production should begin by the end of 1954, and it is planned to ship 10,000,000 tons of ore from Seven Islands during a nine months season.—A. G.

Ontario Annual Review—1952. J. C. Browning. (*Canad. Min. J.*, 1953, **74,** Feb., 94–100). Ontario's mineral production lagged slightly in 1952 but the district is becoming a major source of iron ore, with a target for 1955 of 1,500,000 tons. The Algoma and Bethlehem Steel Corporations are developing the Michipicoten and Marmora deposits respectively. A deposit of 60,000,000 tons of high grade magnetite is reported 100 miles northwest of Sudbury.—A. G.

Estimate of the Reserves of Iron Ore in Brazil and the Geographical Distribution of the Deposits. Luciano J. de Moraes. (*Bol. Assoc. Brasil, Metais*, 1952, **8,** Oct., 389–407). [In Portuguese]. The author reviews estimates of the deposits of iron ore in Brazil. (96 references).—R. S.

ORES—MINING AND TREATMENT

Report of Conference on Imported Ore Handling. (Brit. Iron Steel Fed.: *J. Iron Steel Inst.*, 1954, **176,** Jan., 66–70). [This issue].

Significance of the Mechanism and Rate of Collecting for Intensification of the Flotation Process. V. A. Glembotskii. (*Izvestiya Akademii Nauk SSSR, Otdelenie Tekhnicheskikh Nauk*, 1950, (2), 253–258). The nature of the interaction between molecules of a collector and the surface of mineral particles is discussed. An investigation of flotation rates revealed that the approximate velocity of the collecting reaction and the distribution of mineral particles in accordance with their chemisorptive activity can be estimated. The collecting reaction is not instantaneous, but it cannot be classified as a slow one.—V. G.

Recent Improvements in Flotation of Oxide Manganese Ores. J. B. Rosenbaum and C. H. Schack. (*Mines Mag.*, 1953, **43**, Mar., 67–69). Details are given of laboratory and pilot-plant work by the U.S. Bureau of Mines on ores of 10·6% Mn content. About 80% of the manganese was recovered in a 34–35% concentrate. The method was used, with modifications, for many other ores. An oil emulsion procedure is more widely applicable than dispersed flotation. It depends on prolonged conditioning preceding manganese flotation, using 10–150 lb. of oil per ton of ore. A mixture of tall oil and diesel oil, with a wetting agent, is utilized.—K. E. J.

Manufacture of Low-Arsenic Sinter from the Kimobetsu Ore (Hokkaidô). T. Ikeno and T. Hagiwara. (*Tetsu to Hagane*, 1953, **39**, Feb., 166–168). [In Japanese]. This is a review of sintering processes generally, and operations and equipment at one plant. (30 references).—K. E. J.

Contribution to the Theory of Milling Processes. K. Sedlatschek and L. Bass. (*Powder Met. Bull.*, 1953, **6**, May, 148–153). A mathematical theory to describe the milling process (*e.g.*, ball milling) is put forward. It improves on previous explanations (*e.g.*, the Rosin–Rammler equation) since empirical elements are eliminated, the limits of applicability can be stated *a priori*, weight-percentages of the fractions are related to milling time, and the initial particle size distribution is taken into consideration.—K. E. J.

An Experimental Study of the Rejection of Phosphorus from Iron Ore by Magnetic Separation. K. Kanazawa and K. Yabuuchi. (*Kyoto Univ., Bull. Eng. Res. Inst.*, 1952, **2**, Sept., 44–47). [In Japanese]. Details are given of concentration processes, with a Davis magnetic-tube concentrator, used on Tojo ore (Fe 48·99%, P 0·0167% and SiO_2 29·03%). With regrinding of ore fraction, ore of >60% Fe and <0·01% P and 10% SiO_2, suitable for making low-phosphorous pig, was obtained at about 90% iron recovery.—K. E. J.

Sintering of Pelletized Iron Ore. Z. Krotkiewicz and B. Sewerynski. (*Biuletyn Informacyiny Instytutow Ministerstwa Hutnictwa*, 1953, **4**, (8), 29–32.; *Hutnik*, 1953, **20**, (8)). [In Polish]. The mechanism of sintering iron ore pellets is discussed and the main types of furnace used are reviewed. A description of an experimental circular tunnel furnace with a rotating hearth, designed by the Polish Institute of Metallurgy, for the ignition of 1½ ton/hr. of pellets is briefly described.—V. G.

Study of the Movement of Grains on Ore on Shaking Tables. E. Mercuri. (*Ric. Sci.*, 1953, **23**, May, 841–848). [In Italian]. The author examines the conditions which determine the sliding of grains on ore concentration tables and puts forward formulæ to explain their motion. A special study is made of the conditions under which grains are lifted from the table by acceleration.—M. D. J. B.

Progress in Ironmaking Research. (*Brit. Steelmaker*, 1953, **19**, Aug., 486–491). **Research in Ore Preparation and Steelmaking : Pelletizing and Sintering Investigations.** (*Iron Coal Trades Rev.*, 1953, **167**, July 24, 189–191). **Sintering and Pelletizing.** (*Iron and Steel*, 1953, **26**, Aug., 395–396). A summary is given of research on ore preparation and blast-furnace experiments carried out by B.I.S.R.A. in co-operation with ironmaking firms in the North-East Coast area. The subjects covered include pelletizing, sintering, fuel compositions, radioactive tracers for determining gas transit times, carbon hearths, and under-hearth cooling.—G. F.

Evolution and Present Development of Lime Kilns Particularly for the Production of Lime for Steel Making. K. Guthmann. (*Radex Rundschau*, 1952, (4), Aug., 141–160). The development of annular, shaft, and rotary lime kilns is surveyed, and shaft kilns are discussed in detail. The use of solid, liquid, and gaseous fuels is described. Various recent kilns fired with blast-furnace gas are closely studied and compared. Full data relating to performance and life are quoted.

FUEL—PREPARATION PROPERTIES AND USES

National Fuel and Energy Resources and Their Efficient Utilization. A. Parker. (*Claycraft*, 1953, **26**, June, 430–434). A brief statistical record on a national basis is given of the production, consumption, and efficiency of utilization of such fuel and energy resources as coal and lignites, oils (petroleum and shale), natural gas, peat, wood, radiation from the sun, waterpower, and wind power.—J. R. P.

Combustion and Gasification of Carbon Considered as a Chain Reaction. H. Behrens. (*B. W. K.*, 1953, **5**, Aug., 272–275). On the basis of the thermodynamic evaluation of the temperature below which formation of water-gas becomes impossible, it is shown that the deposition of carbon and the generation of water-gas can be accounted for, in agreement with measurements, if both are assumed to be chain reactions with the H- and OH- radicals as links. The results are applied to the gasification of coal dust as an example.—P. F.

A Universal Gasification Triangle. S. Traustel. (*B.W.K.*, 1953, **5**, Aug., 261–264). A monogram is developed by the aid of which the relation between the CO_2, CO and oxygen contents of flue gas can be utilized for the determination of the excess air required for combustion, not only for one particular fuel, but for any type of fuel. The chart is reproduced.—P. F.

General Diagram for Fuels. W. Boie. (*Technik*, 1953, **8**, May, 305–309). It is shown how the properties of sulphur-free fuels may be summarized in a hydrogen-oxygen diagram. For this purpose the author establishes characteristic coefficients, the values of which are given for a series of liquid and solid fuels. The diagram enables one to read off theoretical amount of air for combustion.—J. G. W.

Sulphur in Fuel and the Dew-Point of the Flue Gas. W. Gumz. (*B.W.K.*, 1953, **5**, Aug., 264–269). Starting with the sulphur content of the fuel with the subsequent formation of SO_3 and the catalytic influence of adsorbing solid particles and soot on this process, the formation of sulphuric acid is examined on a thermodynamic basis. The dew-point of a sulphuric acid and water-vapour mixture lies considerably above that of pure water vapour, but the formation and precipitation of the acid is nevertheless prevented by the high degree of dilution. An exact mathematical treatment of the problem is difficult, and new measurements do not provide a definite answer. Practical possibilities for developing the dew-point method for estimating sulphur in exhaust gases are briefly discussed.—P. F.

The Calculation of Radiant Heat Absorption in a Furnace. I. Granet. (*J. Amer. Soc. Naval Eng.*, 1953, **65**, May, 319–327). The problem of the calculation of the radiant heat absorbed in furnaces is considered in detail with particular reference to oil-fired furnaces. (17 references). B. G. B.

Heat-Capacity Standards. (*Indust. Heating*, 1953, **20**, June 1076–1078). The use and development of benzoic acid, *n*-heptane aluminium oxide and diphenyl ether as new heat-capacity standards in calorimetry is considered. Their useful ranges are compared with that of water.—B. G. B.

Vanadium Ash Problems in Oil Fired Boilers. F. E. Clarke. (*J. Amer. Soc. Naval Eng.*, 1953, **65**, May 253–270). An account of several cases of severe slagging in oil-fired boilers due to the presence of vanadium in the fuel oil is given. The slag deposits, which contain vanadium compounds, are examined and their formation discussed. Research work on the mechanism of slag formation and on the constitution of oil fuels in considered to be needed.—B. G. B.

Flexibility in Air-Gas Mixing. A. D. Wilcox. (*Indust. Heating*, 1953, **20**, June, 1082–1090). The development of low-pressure proportional air-gas mixers for gas-fired furnaces is reviewed. The latest design of mixer is described and this can be adapted for use under widely varying conditions. By a simple adjustment of the mixer after installation, the maximum efficiency possible on each particular installation can be easily achieved.—B. G. B.

Sampling of Granular Fuels. Ideas on Standardization. K.–V. Otto. (*Glückauf*, 1953, **89**, July 4, 690–692). Difficulties of standardized sampling, due to variations in materials are outlined, and the extent to which a degree of standardization is possible is discussed.—L. D. H.

Flow Distribution in Packed Beds. C. E. Schwartz and J. M. Smith. (*Indust. Eng. Chem.*, 1953, **45**, June, 1209–1218). Data obtained in pipe sizes from 2 to 4 in. showed that a peak gas velocity occurred at approx. 1 pellet diameter from the wall. For $D_t/D_p < 30$, this velocity was 30–100% greater than that at the centre. Unless this ratio >30, velocity variations will exist, and may be important for the operation of catalytic reactors and packed-bed heat exchangers. (17 references).—K. E. J.

Non-Uniform Heat Transfer to Fluids Flowing in Conduits. V. J. Berry, jun. (*Appl. Sci. Res.*, 1953, **4**, Section A, (1), 61–75). The general theory of temperature distribution in a fluid flowing in a heated conduit is discussed. Equations

are derived for temperature distribution throughout the fluid stream and an expression is presented for the Nusselt modulus as a function of downstream position. The asymptotic value of the Nusselt modulus is shown to depend upon system geometry and hydrodynamics, and temperature boundary conditions. A simple procedure is given computing the heat transfer coefficient for round pipes and parallel wall conduits.

Considerations on Heat Exchangers. A. Huet. (*Soc. Roy. Belge. Ing. Bull.*, 1951, Oct., 236–242). Methods of improving heat transfer in heat exchangers are discussed. A number of tubular heat exchangers of novel design are described and illustrated.—B. G. B.

New Designs of Cast-Iron Recuperators. H. Weineck. (*B.W.K.*, 1953, **5,** July, 229–234). Recent designs of recuperators used in forges, for heating blast-furnace blast, for use with cupolas and with furnaces supplying drying air in the manufacture of refractories, are described, and the economics of their performance are discussed. A turbo-air-preheater, having a heating surface of about 1000 sq. ft. is described.

Steelworks Waste-Heat Boiler Practice. R. McDonald. (*J. Iron Steel Inst.*, 1954, **176,** Jan., 71–92). [This issue].

Coking Coals of North Staffordshire. H. J. Crofts. (*Trans. Inst. Min. Eng.*, 1953, **112,** June, 719–732). Based on new evidence from recent borings on account is given of the structure of the North Staffordshire coal field and of the depths, qualities, and reserves of the coking seams. New information from the Cannock and Shropshire coal fields is included.—E. C.

The Routine Sampling of Coal. R. C. Tomlinson. (*J. Inst. Fuel*, 1953, **26,** Aug., 83–91). The principles of sampling are discussed, and practical methods of finding an economical scheme and checking its accuracy are given. The sample must be free from bias ; duplicate sampling allows accuracy to be assessed. Sampling from small quantities measures variability of the supply.—D. L. C. P.

The Use of "Random Numbers" in the Theory of Coal Sampling. A. B. Manning. (*J. Inst. Fuel*, 1953, **26,** Aug., 107–108). This is a method of calculating the error of a coal sample by dividing it, on paper, into say five ' float and sink ' samples, and determining the variance in ash content of random samples divided similarly. This compares with an earlier method which divides the sample into coal, middlings, and dirt only.—D. L. C. P.

The Design and Construction of a Transportable Fine Coal Cleaning Plant. D. H. Gregory and P. F. Whelan. (*Trans. Inst. Min. Eng.*, 1953, **112,** June, 767–781). Conditions necessitating the use of transportable fine coal treatment units are outlined and a prototype plant, producing 5 tons/hr. of clean coal, is described. The plant comprises units for the repulping of fine coal, separating coal and shale by froth-flotation, and dewatering the clean coal on jigging screens and a porous belt.—E. C.

Dense Medium Processes for Coal Cleaning. F. F. Ridley and H. Y. Robinson. (*Colliery Guardian*, 1953, **187,** Aug. 6, 189–194 ; Aug. 13, 221–225). The processes at present being used commercially in Great Britain to clean coal by flotation in a dense medium and some other processes used abroad are reviewed and discussed.—B. C. W.

Reducing the Moisture Content and Large Water Variations in Russelton Washed Coal. O. R. Lyons. (*Min. Eng.*, 1953, **5,** June, 614–619). Addition of small amounts of light oil to $-\frac{1}{4}$ in. raw coking coal, before wet tabling, did not appreciably reduced the moisture content of the cake from a Bird centrifuge, although ash content was lowered.—K. E. J.

Research and Development in the Chemistry of Coal. O. Grosskinsky. (*Z. V.d.I.*, 1953, **95,** May 15, 415–421). This is a review of post-war developments in the Ruhr, covering coking, low-temperature carbonization, gasification, Fischer Tropsch process, and utilization of by-products.—J. G. W.

Progress in and Problems of Coking Practice. W. Gollmer. (*Z. V.d.I.*, 1953, **95,** May 15, 407–414). The author surveys the rehabilitation of West German coking plants since the war and discusses their present-day problems, particularly with reference to available coal, in the light of latest technical achievements.—J. G. W.

Investigations into the Influence of Additions of Sodium Compounds upon the Process of Semicoking of Coals. M. B. Ravich, V. A. Lanin, and V. I. Korshunov. (*Zhurnal Prikladnoi Khimii*, 1951, **24,** (9), 970–975). The influence of sodium hydroxide, sodium carbonate and sodium chloride additions to the coal charge on the yield of liquid and gaseous products during low-temperature carbonization was investigated.—V. G.

Rates of Heat Consumption in a Modern Coke-Oven Plant. D. Sandulli. (*Calore*, 1953, **24,** Mar., 118–132). [In Italian]. The author describes the new coke-oven plant of Societa Vetrocoke at Porta Marghera and tests carried out to determine the consumption in calories per unit weight of coal. These showed that consumption was within the guaranteed limits stipulated by the contractors.—M. D. J. B.

The Purification of Carbonisation Effluents. T. H. Williams, H. M. Spiers, and E. I. Akeroyd. (*Coke Gas*, 1953, **15,** July, 245–252). Details are given of experiments carried out on a pilot plant for the treatment of liquor produced in coke-oven practice. The free ammonia is removed by steam distillation, and after cooling, the liquor is passed through an ion-exchange resin to remove the thiocyanate and thiosulphate. This is followed by treatment with active carbon to remove phenol, the higher tar acids, and the colour forming constituents. The phenols can subsequently be concentrated into a saleable product. The final liquid is water-white and suitable for discharge into waterways. Full details are given of the operation of the plant and of the regenerationg procedure used for both the ion-exchange resin and the activated carbon. Various aspects of the process are covered by patents.—B. C. W.

On the Iron Introduced from Apparatus on Crushing the Coke Sample. T. Iwahashi, I. Kawahata and I. Hatakeyama. (*Tetsu to Hagane*, 1953, **39,** Jan., 50–56). [In Japanese]. Contamination of daily works coke samples led to values of Fe_2O_3 in the ash being some 3% too high. Crushing in agate mortars, or removal of Fe_2O_3 by magnet, removed the error, but for works practice grinding by pounding proved most convenient.—K. E. J.

Firing Tests with Coke Dust. H. Winter and R. Jüterbock. (*B.W.K.*, 1953, **5,** Aug., 275–280). A description is given of a prolonged investigation of the applicability of coke dusts of various particle sizes for combustion in high-pressure boilers. It is shown that, with the improvements described, it is possible to utilize coke dust as boiler fuel giving adequate efficiency and no ignition difficulties.—F.

Some Studies on Reativity of Coke. H. Jo, S. Ida, and H. Yukiura. (*Tetsu to Hagane*, 1953, **39,** Apr., 379–384). [In Japanese]. Reactivity tests in CO_2 atmospheres are reported. Variation between 4 and 8 hr. in heating time from 20 to 1200° C. produced no noticeable effect on reactivity. Reactivity of normal coke was higher than that of coke made from a blend including some coke breeze. —K. E. J.

Automatic Control of Gas Producers. (*Metallurgia*, 1953, **47,** June, 287). In the Kent scheme, which is described, the gas off-take temperature is detected by a thermocouple. It is measured by a potentiometric temperature recorder containing a three-term pneumatic controller, whose output signal is added to that generated by a load signal transmitter. The combined control signal actuates a coal feed regulator. The full scheme provides for control of gas off-take pressure and blast saturation temperature.—B. G. B.

Pulverized-Coal Gasification—Ruhrgas Processes. K. Traenckner. (*Trans. Amer. Soc. Mech. Eng.*, 1953, **75,** Aug., 1095–1101). The general programme of research and development of the Ruhrgas A-G. is explained. Main efforts were directed to the development of two gas producers using low-grade pulverized coal or coal dust from coal cleaning operations—D. H.

Progress in the Practice of Long Distance Gas Supply. W. Wunsch. (*Z. V. d.I.*, 1953, **95,** May 15, 422–428). This is an up-to-date survey of the German gas grid. Developments discussed are compression plant, design of transmission lines and dust control. Reference is also made to instrumentation and to automatic control of gasometers.—J. G. W.

TEMPERATURE MEASUREMENT AND CONTROL

Designing an Accurate Immersion Thermocouple. R. E. Bish. (*Foundry*, 1953, **81,** Aug., 193, 244). The use of immersion thermocouples and the embrittlement of Pt/Pt-Rh couples are considered. Details are given of a thermocouple assembly designed to minimize mechanical breakage and embrittlement, and to give an accurate measurement of liquid steel temperatures.— B. C. W.

Thermoelectric Installation for High Accuracy Temperature Measurements, Particularly for Thermal Analyses. W. Hunsinger. (*Z. Metallkunde*, 1953, **44,** June, 261–264). The

instrument described measures the thermoelectric current by the use of a photocell compensator and a pen recorder. Modifications are described which give an accuracy of $\pm 0{\cdot}05\%$ at 1000° C.—L. D. H.

On the Temperature Sensitivity of Special Magnetic Materials. T. A. Heddle. (*Brit. J. App. Phys.*, 1953, **4,** June, 161–166). Magnetic materials sensitive to temperature changes between −60° and +120° C. are surveyed, and their use in temperature detecting and compensating devices is considered.

Automatic Control of Hot Blast Temperature. G. Olah and R. Andrews. (*Elliot J.*, 1953, **1,** May, 104–109, 112). A description is given of an automatic control, constructed by the Elliott Company, for the temperature of the hot blast for blast-furnaces. A hydraulic actuator is used to operate the hot blast control valve and an electric measuring and transmitting system is employed. Full details of the equipment are given.—B. G. B.

REFRACTORY MATERIALS

Vapour Pressure/Moisture Characteristics of Clays and Their Relation to Plasticity and Bonding Properties. B. Vassiliou and J. White. (*Trans. Brit. Ceram. Soc.*, 1953, **52,** July, 329–385). A critical examination is made of existing data to ascertain the relative importance in bonding of the factors particle size, particle shape, and the ability of the clay to hold to its surface relatively 'thick' films of moisture. A new method of investigating vapour pressure relationships has been devised, depending on the observation that, in a clay mass exposed to a temperature gradient, movement of moisture occurs towards the cooler portion of the mass. Such effects are accounted for on the basis of the Kelvin equation for capillary condensation and in terms of alternative mechanisms of adsorption. Vapour-pressure isotherms for the various clays studied have been constructed. At low relative vapour pressures, surface adsorption predominates; at higher vapour pressures, capillary condensation and thickening of the films due to osmotic activity of the exchangeable cations both contribute to the observed adsorption.—J. R. P.

Effect of Additional Pugging on Clays and Shales. A. P. Steele, jun. (*Amer. Ceram. Soc. Bull.*, 1953, **32,** June, 215–217). The distinction between "pugging" and "mixing" is made clear. The possible benefits of curing the clay or introducing heat into the pugmill or a straight-line machine with shredder and auger for compression are considered.—J. R. P.

Physicochemical Studies on Dusts. VI—Electron-Optical Examination of Finely Ground Silica. J. G. Gibb, P. D. Ritchie, and J. W. Sharpe. (*J. Appl. Chem.*, 1953 **3,** May, 213–218). Removal of the high-solubility surface layer from crystalline quartz and fused silica dusts with 40% HF and from Lochaline sand dusts by a borate buffer (*p*H 7·5) brought about changes in electron-diffraction which show that this layer is amorphous (estimated mean thickness 0·03–0·06 μ).

The Production and Application of Refractories from Stabilized Dolomite. W, Szymborski and K. Elsner. (*Hutnik*, 1953, **20,** (6) 194–197). [In Polish]. The production of refractories from stabilized dolomite by the method evolved by the Polish Institute of Metallurgy, and the properties and application of these refractories are described.—V. G.

On the Crystal Structure of Montmorillonite, with some References to Other Clay Minerals. M. Nakahira. (*J. Sci. Res. Inst.*, 1952, **46,** Dec., 268–287). [In English]. Results of powder X-ray studies are presented. The crystal structure of montmorillonite is built up from parallel but randomly-spaced pyrophillite layers. Water molecules introduced variations in spacing. Unit cell dimensions are given. The inter-layer spacings of halloysite and montmorillonite are larger than those of kaolinite and pyrophillite, which have less disordered structures. (12 references).—K. E. J.

Permeability and Some Other Properties of a Variety of Refractory Materials. I. G. B. Massengale, L. E. Mong, and R. A. Heindl. (*J. Amer. Ceram. Soc.*, 1953, **36,** July, 222–229). Flat, edge and end permeabilities, bulk densities, moduli of elasticity, and porosities were determined for various types of refractory brick as received from the manufacturers. These properties were determined also for samples of unburned chrome-magnesite and magnesite-chrome brick after heat-treating at 925° and 1600° C., and also for samples of clay pots after heating at various temperatures.—J. R. P.

Reaction of Zinc and Zinc Oxide with Firebricks. H. M. Richardson and G. R. Rigby. (*Trans. Brit. Ceram. Soc.*, 1953, **52,** Aug., 405–416). It is considered that the deposition of metallic zinc or zinc oxide in the brickwork of blast-furnace stacks would not cause serious disintegration. It is shown that zinc oxide reacts with firebricks between 800° and 1000° C. to form zinc silicate and zinc aluminate, and that above 1000° C. zinc silicate and mullite do not occur together. Zinc oxides reacts with fayalite at 800° C. in nitrogen to form zinc silicate and ferrous oxide, and the mixture is reactive towards carbon monoxide; it is suggested that this reaction may account for the deposition of carbon in blast-furnace stacks. —J. R. P.

The Electrical Conductivity of Spinels. T. E. Bradburn and G. R. Rigby. (*Trans. Brit. Ceram. Soc.*, 1953, **52,** Aug., 417–435). A brief survey of the possible mechanisms of conduction in spinels is given. An apparatus for measuring the conductivity of spinels at temperatures up to 1000° C., including a specimen holder of heat-resistant steel, is described. The results of experiments on cobalt aluminate, cobalt chromite, magnesium aluminate, magnesium chromite, magnesium ferrite, nickel aluminate, nickel ferrite, zinc aluminate, zinc chromite, zinc ferrite, ferrous chromite, and magnetite are given, and the probable method of conduction in each case is suggested.—J. R. P.

Thermo-Differential Precision Analysis. P. Spinedi and O. Franciosi. (*Ric. Sci.*, 1952, **22,** Dec., 2323–2338). [In Italian]. The authors discuss the capabilities and limitations of the modern Micromax and Speedomax temperature recording apparatus for the study of transformations in refractory materials. The influence exercised by different factors on the form and development of the differential curves is analysed, and the quantitative and qualitative results with tests on clay and calcium carbonate are reported and discussed.

The Formation of Magnesium Hydroxide in Sintered Magnesite. H. Schreiner. (*Radex Rundschau*, 1952, (6), Nov., 255–260). The adsorbtion of radioactive tracers from aqueous solutions and gases, X-ray, and microscopic examinations are used to investigate the process of hydration of dead-burnt magnesite. Hydration was found to start at reactive centres then spreading over the surface of the periclase crystals, thus destroying the brick structure. The end product has a brucite lattice.—E. C.

The Examination and Properties of Refractory Materials. G. van Gijn. (*Chem. Week*, 1953, **49,** Jan. 24, 53–58). [In Dutch]. The author outlines the laboratory tests usually conducted on refractory materials, pointing out that the results obtained are often inapplicable to practical conditions. As long as there is insufficient knowledge of the fundamental factors influencing the refractoriness of the material, often the only alternative is to try it out under practical conditions in close collaboration between the manufacturer and the user.

Improvements in Refractories of Iron and Steel Industry. S. Mori. (*Tetsu to Hagane*, 1953, **39,** Apr., 449–457). [In Japanese]. This is a review of recent trends in refractories for open-hearth and blast furnaces, and ladles, particularly in the U.S.A. (12 references).—K. E. J.

Comparison of Costs of Chrome-Magnesite and Silica Linings for a 70-ton Open-Hearth Furnace. K. O. Zimmer. (*Radex Rundschau*, 1952, (6), Nov., 227–234). Experiences made during a furnace campaign with an all-basic lining are discussed. Economic and metallurgical advantages of chrome-magnesite linings are described, lower materials and maintenance costs, increased production and better desulphurization due to higher working temperatures being claimed.—E. C.

The Neston Works of Morgan Refractories, Limited. (*Engineering*, 1953, **175,** June 12, 757–758: *Engineer*, 1953, **195,** June 12, 836–837; *Metal Ind.*, 1953, **82,** 836–837; *Iron Coal Trades Rev.*, 1953, **166,** June 5, 1287–1288; *Brit. Steelmaker*, 1953, **19,** July, 416–420; *Eng. Boilerhouse Rev.*, 1953, **68,** July, 206–210; *Iron Steel*, 1953, **26,** July, 357–759; *Steam Eng.*, 1953, **22,** July, 392–396; *Ceramics*, 1953, **5,** July, 211–216). A new works covering 43 acres has been opened at Neston by Morgan Refractories, Ltd. with plant for production by modern methods of specialized refractories, including the 'M.R.' series of aluminous refractories and 'M.I.' series of insulating refractories. Among the latter is the 'M.I.28' brick which withstands face temperatures of 1540° C. The new works is described.—R. A. R.

BLAST-FURNACE PRACTICE AND PRODUCTION OF PIG IRON

New Smelting Techniques in the Iron Industry and Their Influence on the Construction of Iron and Steel Works. G. Bulle. (*Z.V.d.I.*, 1953, **95,** May 15, 435–440). Post-war developments intended to bring the German steel industry into line with other countries are described. Reference is made to plans for blast-furnaces of 1300–1700 tons/day production capacity, of integral construction ; to high top pressure and oxygen-enriched blast ; low shaft furnaces ; the manufacture of pig iron from scrap ; and ore preparation. Developments in steelmaking are concerned with oxygen blown Bessemer converters and open-hearth furnaces. Continuous casting is briefly touched upon.—J. G. W.

The International Low-Shaft Furnaces at Liège. P. Coheur, M. Fouassin, and E. Frenay. (*Rev. Univ. Min.*, 1953, 9th series, **9,** Aug., 482–492). A detailed description of the design and construction of the low-shaft blast-furnace at Liège is given. The furnace is designed to produce 60–100 tons of iron per day. Diagrams of the plant layout and of the furnace are reproduced together with 21 photographs taken during the construction. Blowing-in took place on May 13, 1953. No details of the performance are given.—B. G. B.

Smelting Iron Ore in Low Shaft Furnaces. K. Säuberlich. (*Met. u. Giesserei Techn.*, 1952, **2,** May, 139–140). Tests in a 3–4 ton furnace were undertaken to ascertain the results of smelting ores with mixtures and briquettes of low grade fuels to produce foundry iron, and the results were studied as a basis for the operation of the low shaft furnace to be constructed at Calbe a. d. Saale. Brown coal briquettes were unsatisfactory, but a high-sulphur iron was obtained with a mixture of these briquettes and Zwickau coke, and the sulphur content was reduced by increasing the blast temperature, increasing the amount of slag, and desulphurizing additions.—R. A. R.

Blast Furnace Plant Reconstruction at Sheepbridge : Latest Equipment Incorporated in an Efficient Layout. T. Bishop. (*Iron Coal Trades Rev.*, 1953, **167,** Sept. 11, 581–589). Extensive reconstruction of the blast-furnace and associated plants has recently been made at the Chesterfield works of the Sheepbridge Co. Ltd. The layout, ore-handling and crushing plant, coke-screening and handling plant, furnace-charging equipment, blast-furnaces, hot-blast stoves, hot-metal and slag lines, blast-furnace gas system, and other ancillary services are described.—G. F.

Limit of Desulphurization of Liquid Pig Iron of Fe–C–S System with Solid Lime and Calcium Carbide. H. Sawamura. (*Tetsu to Hagane*, 1953, **39,** Jan., 17–22). [In Japanese]. The relations between equilibrium values of carbon and sulphur in the iron, and temperature, are calculated. The limit of desulphurization with lime is very low, and decreases with increase of carbon in the iron, if temperature and CO partial pressure are constant. That for solid CaC_2 is also low, decreasing with carbon content of the iron. From the reaction $CaO + 3C = CaC_2 + CO$, the limit of desulphurization with lime is generally greater than that with CaC_2. (20 references).

The Electric Smelting of Iron. M. Dabala. (*Mét. Constr. Mécan.*, 1953, **85,** June, 447–467). A detailed account of the development of the electric smelting method for the production of iron from iron ores is given. The operational performance of many of the furnaces used is considered. The chemical reactions which occur during smelting and the slag compositions used are discussed. The electric smelting process is considered to be suitable for the manufacture of any grade of iron.—B. G. B.

The Influence of the Nitrogen Partial Pressure in the Blast on Nitrogen Pick-up. T. Kootz. (*Arch. Eisenhüttenwesen*, 1953, **24,** May–June, 203–206). When blowing a converter with a blast low in nitrogen, the influence of a lower nitrogen saturation limit at the start of the nitrogen pick-up is outweighed by that of the reduced supply of nitrogen. The observation that, with increasing dilution of the nitrogen by oxygen enrichment of the air blast, the nitrogen pick-up in practice is higher than that calculated is attributed to the fact that increasing oxygen concentration increases the gas-metal interface temperature and so over-rides the influence of the reduced nitrogen supply. According to calculations, denitriding during carbon removal is possible only if a part of the carbon in the bath is burned out by iron oxide in a region remote from the gas stream.—J. P.

Rapid Elimination of Scaffolding and the Bear in Blast-Furnaces. M. Aybar Gallego. (*Inst. Hierro Acero*, 1953, **6,** Apr.–June, 103–116). [In Spanish]. The author explains the causes of scaffolding and analyses the methods most used for its elimination. Explosive methods of cleaning the stack and the addition of sodium carbonate to the charge are given special attention. The method of removing the bear in liquid form is described and compared with the use of explosives.—R. S.

Cleaning Blast-Furnace Gas at the Vereinigte Oesterreichische Eisen- und Stahlwerke at Linz. A. Uxa. (*Stahl u. Eisen*, 1953, **73,** July 16, 975–980). The plant, construction, and operation of the wet electro-filter blast-furnace-gas cleaning plant at the above works are described. Works' tests have shown that dust contents in the cleaned gas of less than 10 mg./cu. m. can be obtained with a mean current consumption of only 0·36 kWH./1000 cu. m. Very good cleanliness was also obtained under the difficult operating conditions of high lead and zinc contents in the dust and over-loading of the plant.—J. P.

The Use of Sonics and Ultrasonics for Gas Cleaning. H. Schnitzler. (*Arch. Eisenhüttenwesen*, 1953, **24,** May–June, 199–202). The principles of sonic gas cleaning are presented and experiments on the flocculation of aluminium and magnesium oxide smokes by the use of a siren are described. Because of the high energy consumption of modern sound generators their use for gas cleaning is not justified. The gas required to drive a siren amounts to 25–35% of the volume of the gas to be cleaned and the driving gas will itself have to be cleaned. The installations will require to be sound-proofed and the sonic energy in the cleaned gas will have to be damped. These facts suggest that sonic cleaning has no very bright future.—J. P.

TREATMENT AND USE OF SLAGS

The Presence of Gehlenite in Granulated Blast-Furnace Slags. M. I. Strelkov. (*Doklady Akademii Nauk S.S.S.R.*, 1953, **90,** (3), 441–443). [In Russian]. To verify statements in the literature that granulated blast-furnace slags contain gehlenite, the velocity and degree of chemical reaction between calcium sulphate and this slag were investigated. Some samples were also studied by the microscope and X-rays. It is concluded that : (1) Gehlenite is not formed in normally granulated blast-furnace slags ; (2) the trisulphate form of calcium sulphate-aluminate is produced during the interaction of slags with gypsum in saturated solutions ; (3) During boiling of the slag in lime-gypsum solutions, the monosulphate form of calcium sulphate-aluminate is produced and this crystallizes in plates which at room temperature quickly transform into needles.—V. G.

Sydney Foamed Slag as a Lightweight Aggregate. M. R. Foran, S. Ball, R. E. Johnson, and J. R. Wallace. (*Eng. J.*, 1953, **36,** May, 566–572). Many properties of foamed blast furnace slag produced by Dominion Iron and Steel Co., Ltd., have been determined, and their engineering significance is discussed. For the aggregate, tests included nature of impurities, sieve analysis, durability, mortar-making properties, thermal conductivity and chemical behaviour. For lightweight concrete, data are given for strength, density, conductivity, volume changes, resistance to impact, load, freezing and thawing, moisture penetration and acoustic properties. Its use in construction is described. (12 references).—K. E. J.

Hydraulic Properties of High Alumina Slags in Relation to Their Phase Characteristics. I. Z. Volchek. (*Doklady Akademii Nauk S.S.S.R.*, 1953, **90,** (3), 437–440). [In Russian]. A study of the hydraulic properties of high alumina (46–50%) slags in relation to their phase composition is reported. Variations in phase composition were obtained by varying the cooling rate of fused slags. The results showed that glassy slags possess a considerable hydraulic activity. It was also shown that the hydraulic activity of some slags can be considerably increased by suitable conditions of crystallization.

PRODUCTION OF STEEL

The Royal Netherlands Blast Furnaces- and Steelworks: The New Rolling Mills for Thin Plate and Sheet at Ijmuiden. A. H. I. Housz, A. Drijver, A. J. van Walraven, E. Voet, and C. M. R. E. Smulders. (*Iron Coal Trades Rev.*, 1953, **167,** Sept. 18, 625–651). A detailed description is given of the new

plate, sheet, and strip mill at Ijmuiden. Civil engineering aspects, including preparation of the site, foundations, excavations, and drainage, are first considered, followed by descriptions of the slabbing-blooming mill, hot-strip mill, and cold-rolling mill, with attention being drawn to factors influencing rolling. The soaking pits, slab reheating furnaces, and annealing furnaces are next described and processing details are given. Finally, the works services are outlined and the electrical installations and mill drives are discussed.—G. F.

Royal Netherlands Steelworks: Formerly J. M. de Muinck Keizer, Limited, Utrecht. (*Iron Coal Trades Rev.*, 1953, **167,** Sept. 18, 659–662). Following a brief history of the firm, an account is given of post-war development at the Royal Netherlands Steelworks near Utrecht. The melting shop, steel castings foundry, rolling mills, cold-machining section, wire-drawing department, and the forge are described.—G. F.

Operations at the Works of N. V. Nederlandsche, Kabelfabriek. (*Iron Coal Trades Rev.*, 1953, **167,** Sept. 18, 653–658, 663). This article describes the layout and sequence of operations at the Alblasserdam works of the Netherlands Cableworks Ltd. Details are given of the steelworks, with three 35-ton open-hearths furnaces and two 25–30 ton electric furnaces, and of the continuous billet, strip, and rod mills.

Youngstown Sheet and Tube Company Increases Service to the Midwest. C. Longenecker. (*Blast Furn. Steel Plant*, 1953, **41,** Aug., 898–925). A comprehensive account is presented of the activities and plant of the Youngstown Sheet and Tube Co., which is now the sixth largest steel producer in America. Details of coke ovens, blast-furnaces, open-hearth furnaces, rolling mills, pipe mills and tinplate lines are given.

Design Features of Fairless Works Open Hearth. H. A. Parker. (*J. Met.*, 1953, **5,** Aug., 976–978). The author outlines the design of the 275-ton fixed basic open-hearth furnaces at the Fairless Works of United States Steel Corp. Attention is drawn to special features, including large hearth area and regenerative volume, and the provision for rapid charging and flushing, and for speedy rebuilding and patching.

The Development of Quality Control in our Steelworks and Rolling Mills. H. J. Bock. (*Met. u. Giesserei Techn.*, 1952, **2,** June, 178–179). The author describes, in very general terms, the standards relating to various processes in the manufacture of steel that have recently been drawn up in Eastern Germany, and the ways in which it is attempted to correlate performance with these standards.—L. J. L.

Statistical Quality Control and Its Effects at Open-Hearth Shop. S. Kuriyama and T. Suzuki. (*Tetsu to Hagane*, 1953, **39,** Feb., 105–110). [In Japanese]. An account is given of 18 months' experience with control charts at the Tsurumi works of Nippon Steel Tube Co. Initially, many types were used, mainly for analytical purposes, but results in the forms of improvements in technique and cost savings were achieved. The establishment of more complete operation standards should enhance the effectiveness of the method.—K. E. J.

Technical Improvement of the Basic Open-Hearth Operation in Yawata Iron and Steel Works. K. Takeda. (*Tetsu to Hagane*, 1953, **39,** Apr., 385–392). [In Japanese]. Considered from the points of view of improving product quality and decreasing production cost, improvement of operation could be made in the following items : Rationalization of equipment, scrap charging, combustion control, and techniques of furnace practice, casting, and ingot making.—K. E. J.

Reaction Equilibria Between Metal and Slag in Acid and Basic Open-hearth Steelmaking. E. T. Turkdogan and J. Pearson. (*J. Iron Steel Inst.*, 1954, **175,** Jan., 59–63). [This issue].

Comparison of Characteristics of Steel Decarburized with Oxygen and with Millscale. L. Piana. (*Met. Ital.*, 1953, **55,** June, 212–217). A statistical analysis is made of the characteristics of a steel decarburized (*a*) with oxygen, and (*b*) with mill scale. It was found that the method of decarburizing has no influence on the quality of the steel.—M. D. J. B.

Removable Open-Hearth Slag Pocket Bulkhead Doors. R. E. Over. (Amer. Inst. Min. Met. Eng. : *Indust. Heating*, 1953, **20,** June, 1120–1126). A description is given of the design and use of a removable bulkhead to facilitate the removal of slag from open-hearth slag pockets. The door consists of a rigid structural steel frame hinged from the top and lined with fully suspended 9 in. thick basic brick. This door has been in continuous service without repair for 1200 heats. Variations in design are considered.—B. G. B.

The Effect of Pig Iron and Coal on the Performance of the Open-Hearth Furnace. W. Dams. (*Met. u. Giesserei Techn.*, 1952, **2,** May, 145–146). Furnaces of 100 tons were used to determine the optimum relationship between the coal and pig iron additions to the scrap charges. The best results were obtained with 16% pig iron.—R. A. R.

Relation Between Titanium and Sulphur in Steel. T. Saito. (*Tetsu to Hagane*, 1953, **39,** Jan., 29–36). [In Japanese]. With nitrogen, sulphur and carbon present in steel, the affinity of titanium for these elements is in the order given. When the titanium and sulphur contents are approximately equal, stable TiS is formed, and poor sulphur prints result. TiS occurs as light violet-grey microscopic particles, easily distinguished visually, which separate to fine particles and give a laminated structure on hot working. TiS in steel obstructs solution and precipitation of TiC. It prevents hot shortness by sulphur, and titanium may be used in place of manganese to obviate this. (16 references).—K. E. J.

Estimation of Basic Open-Hearth Slag Composition by Its Reflecting Microscopic Structure. T. Akutagawa and K. Horikawa. (*Tetsu to Hagane*, 1953, **39,** Feb., 89–96). [In Japanese]. Microscopic structures of slag pancakes can be classified into four groups, mainly according to basicity. By comparison with standard samples, estimations can be made of basicity (to accuracies of 0·1 or 0·2 according as the ratio $Vp = CaO/(SiO_2 + P_2O_5)$ is $<$ or $>$ 2·5). The time for a test was 10 min. The method can be used in works practice and its accuracy is increased by combination with the pancake test. (13 references).—K. E. J.

Measurement of Equilibrium Reaction Among Aluminium, Oxygen and Carbon in Liquid Iron. Z. Shibata and T. Yagihashi. (*Tetsu to Hagane*, 1953, **39,** Apr., 393–402). [In Japanese]. Calculated values of the deoxidation constant for aluminium are lower than experimental values. Its direct measurement is very difficult. A new method of calculation is based on the equilibria of the reactions between aluminium and CO, and oxygen and carbon. A ternary deoxidation diagram for oxygen, carbon and aluminium is presented. (16 references).—K. E. J.

Activity Coefficients of Oxygen and Phosphorus in Iron–Oxygen–Phosphorus Melts. J. Pearson and E. T. Turkdogan. (*J. Iron Steel Inst.*, 1954, **176,** Jan., 19-23). [This issue].

Silicon-Oxygen Equilibrium in Liquid Iron—A Revision. J. Chipman and N. A. Gokcen. (*Trans. Amer. Inst. Min. Met. Eng.*, 1953, **197** : *J. Met.*, 1953, **5,** Aug., 1017–1018). The authors present a revised treatment of their published data on the silicon-oxygen equilibrium in liquid iron, eliminating the complex relation previously proposed between concentration of silicon and activity coefficient of oxygen in liquid iron. Revised values of the thermodynamic properties of the liquid solution are also presented.—G. F.

Oxygen Solubility in Molten Iron–Chromium and Iron–Chromium–Nickel Alloys. B. V. Linchevskii and A. M. Samarin. (*Izvestiya Akademii Nauk S.S.S.R., Otdelenie Technicheskikh Nauk*, 1953, (5), 691–704). [In Russian]. The influence of chromium on the solubility of oxygen in liquid iron was studied by determining the state of equilibrium in the system : metal-bath/oxide-film/gas phase. It was found that, depending on the chromium content in liquid iron, the oxidation products of chromium in the metal are chromite ($FeO.Cr_2O_3$), chromic oxide, and chromous oxide. The results of metallographic investigations of non-metallic inclusions, the study of inclusions isolated by anodic solution of the alloys, and X-ray analysis of oxide phase, confirm that the products of oxidation of chromium dissolved in liquid iron are $FeO.Cr_2O_3$ and Cr_2O_3. In melts containing above 16% of chromium, an increase in the chromium concentration increases oxygen solubility. This is explained by the formation of chromous oxide soluble in liquid iron. It was also found that nickel increases the oxygen solubility in iron–chromium melts.—V. G.

Precipitators Pass Smoke Control Tests. (*Steel*, 1953, **133,** Aug. 31, 78–80). The successful performance of Cottrell electrostatic precipitators on waste gas from open-hearth furnaces at Torrance works of U.S. Steel Corp. is described. Stack dust discharges averaging 75 lb./hr. were reduced to 2 lb. Particle size from the oil and natural gas fired furnaces is below 3 microns, concentration averages 0·7 grains per standard cu. ft. The electrodes are cleaned by a magnetic-impulse (M.I.) continuous rapping system.—D. L. C. P.

Future of Electric-Arc Furnaces: Requirements for Design and Power. J. C. Howard. (*Iron Coal Trades Rev.*, 1953, **166,** June 12, 1348–1352). The author discusses probable future trends in design and application of electric arc furnaces, dealing with charging, power consumption, rotary regulators, electrode holders, water-cooling, refractories, new techniques in electric and duplex steelmaking, and improved working conditions. It is felt that the use of electric furnaces will be greatly extended in the next few years.—G. F.

Some Problems on the Basic Arc Furnace by Oxygen Blowing. T. Takahashi. (*Tetsu to Hagane*, 1953, **39,** Feb., 97–104). [In Japanese]. Results from test and operational oxygen blowing in 5- and 10-ton arc furnaces are given. Factors influencing decarburization velocity are analysed, the principal being carbon content at melt-down. Dephosphorization was more efficient than with the ore process. Slag condition and oxygen supply rate were the major factors, and temperature a minor factor, affecting this. Oxygen blowing produced more efficient and stable removal of hydrogen gas. Finished steel quality was improved in respect of non-metallic inclusions and grain size.—K. E. J.

Deoxidation and Degasification Practice for Basic Electric Furnace Alloy Steels. A. L. Ascik. (*J. Met.*, 1953, **5,** Aug., 986–990). Referring particularly to basic electric alloy steels, the author discusses the carbon content and steel temperatures as factors in deoxidation, and considers the relationship between deoxidation and hydrogen removal. Specific examples of furnace practice are quoted.—G. F.

The Choice of Deoxidation Method for High-Speed Steels in a Basic Electric Arc Furnace. K. Radzwicki. (*Biuletyn Informacyiny Instytutow Ministerstwa Hutnictwa*, 1953, **4,** (7), 25–28 ; *Hutnik*, 1953, **20,** (7)). [In Polish]. Three methods of deoxidizing high-speed steel were tested : (1) Deoxidation under a white slag by adding electrode carbon powder ; (2) deoxidation under a carbide slag ; and (3) two-stage deoxidation under a white slag first with carbon powder and then with powdered ferrosilicon. The structure, quantity of non-metallic inclusions, and cutting properties of steels produced by these methods were examined. The steel produced by all three methods was of equal quality, but for economic and technical reasons the third method is most suitable because the finishing stage is shorter and the electricity consumption is smaller.—V. G.

Reducing Period in Stainless Steel Melting. H. P. Rassback and E. R. Saunders. (*Trans. Amer. Inst. Min. Met. Eng.*, 1953, **197:** *J. Met*, 1953, **5,** Aug., 1009–1016). The authors survey commercial stainless steel melting practice, with particular reference to the reducing period, and consider the validity in commercial practice of the relations previously derived from small experimental heats. The manner by which the efficiency of the production process may be measured is indicated.—G. F.

Electric Melting Furnaces. A. J. Blackwell. (*Elect. Rev.*, 1953, **152,** May 8, 1041–1044). A brief outline is given of the construction, operation, and applications of electric arc blast furnace, and electric arc and H.F. coreless induction furnaces for the manufacture of steel.—L. D. H.

Hydraulic Arc Furnace Electrode Control. (*Metallurgia*, 1953, **47,** June, 291, 294). The Tagliaferri electrode regulator system is reviewed. Automatic regulation is effected in the following way : The electrode is attached to a piston, which is moved by water under pressure. The water is governed by a valve linked to a piston which is operated by oil pressure on one side, and an opposing spring on the other. The variations in the electrode current are reflected in a movable magnetic core attached by a rod to a piston controlling the oil flow.—B. G. B.

Electrode Spacing in Electric Arc Furnaces. O. Krifka. (*Radex Rundschau*, 1952, (6), Nov., 270–271). Differences in electrode spacing between American and European arc furnaces are discussed in brief, the electrodes in European furnaces being generally arranged on a circle of larger radius. No fundamental advantage is found in either method.—E. C.

Lime and Limestone as Slag Producers in the Electric Arc Furnace. L. Pasker. (*Met. u. Giesserei Techn.*, 1952, **2,** May, 147–148). The use of limestone is advocated for unalloyed heats and for heats requiring a vigorous boil or alloying additions after deoxidation. The advantages of slaked lime as a slag former are that the reaction will take place gradually and control is easier.—L. J. L.

High Frequency Generators. J. Buzik. (*Osterr. Masch. Elektrowirtschaft*, 1952, **7,** Dec., 576–580). An outline is given of the types, operation, and underlying principles of H.F. generators for small furnaces used to make special steels. L. D. H.

Steelmaking in the High-Frequency Furnace. J. Mackievic and J. Zampach. (*Slévárenství*, 1953, **1,** (4), 90–95). [In Czech]. An account is given of the author's experiences in the use of the high-frequency furnace in the manufacture of cast iron, manganese steel, and other high and low alloy steels and non-ferrous alloys, supplemented by a critical survey of the literature. The direction of further developments in the design and use of these furnaces, and the improvement of the refractory linings are considered.—P. F.

Estimation of Basic Open-Hearth Slag Composition by Pancake Test. K. Horikawa. (*Tetsu to Hagane*, 1953, Jan., **39,** 22–28). [In Japanese]. A standard method of preparing a spoon sample of slag from a melt is explained. Surface texture can be classified into five groups, and differences within each group depend on basicity and analysis. By reference techniques, components of any sample may be estimated, the error in basicity being 0·1 or 0·2–0·3 at values $Vp = CaO/(SiO_2 + P_2O_5)$ below or above 2·5. The time required is 2–3 min., without special apparatus, and the method is suitable for process slag control. (28 references).

Rapid Estimation of Iron and Steel Slag (A Review). K. Horikawa. (*Tetsu to Hagane*, 1953, **39,** Feb., 149–165). [In Japanese]. Rapid slag analysis, even at the expense of accuracy, is vital for process control. The review covers rapid chemical analysis, pancake tests, microscopic examination, colorimetry, viscosity tests, measurement of *p*H or conductivity of aqueous slag extracts, spectrographic analysis, and estimation by specific gravity. (70 references).—K. E. J.

Use of Fans in Hot Industries. (*Indust. Heating*, 1953, **20,** June, 1094–1098, 1166). The types and designs of industrial fans available are reviewed. A special fan for ventilating an ingot pouring platform is mentioned. This is a 14-blade axial flow pressure fan which can travel with the pouring ladle. Sources of information on the selection of fans for specific uses are cited.—B. G. B.

Study on Ingot Making Practice II. Y. Nakagawa and M. Soga. (*Tetsu to Hagane*, 1953, **39,** Feb., 111–118). [In Japanese]. A comprehensive study was made of the characteristics and differences between acid and basic open-hearth steel, in connection with the origin of sand cracks during ingot production. Basic steel produced more deoxidizing products, and led to more active corrosion of refractories. The oxidation of basic steel was more pronounced than that of acid steel.—K. E. J.

Examination of a High Sulphur Free-Machining Ingot, Bloom and Billet Sections. D. J. Carney and E. C. Rudolphy. (*Trans. Amer. Inst. Min. Met. Eng.*, 1953, **197,:** *J. Met.*, 1953, **5,** Aug., 999–1008). From sections of a 23 × 35 × 75 in. capped slab ingot and of $7\frac{7}{8}$ in. blooms and $2\frac{1}{2}$-in. billets from a companion ingot, the authors have studied the change in size, shape, and number of inclusions occurring during the rolling of high-sulphur (0·30%) free-cutting steel. The structure of the ingot was generally similar to that of killed steel rather than of low-sulphur capped steel, with the inclusions mainly globular. The inclusion length/width ratio increased about fourfold from ingot to bloom and the size decreased about 60% from ingot to billet. The more plastic siliceous inclusions were elongated on rolling, whilst the sulphide inclusions tended to remain globular.—G. F.

Surface Tears in Alloy Steels. B. Kouřil. (*Hutník* (Prague), 1953, **3,** (6), 122–123). [In Czech.] A study of the formation of surface tears in structural and high-alloy steels showed that : (1) Long reducing periods in the electric furnace promote surface tears ; (2) A low sulphur content, probably only a symptom of excessive reduction in the furnace, was found in steels susceptible to this type of damage ; (3) When the heat time included a change of shift the number of rejects increased ; and (4) if the manganese fell below 0·25% with duplex steel, there was a tendency for longitudinal tears to form. In general, it was concluded that : (1) Stable steels, including low and medium carbon steels and austenitic stainless steels, can be removed from the ingot moulds while red hot and allowed to cool in air, but high alloy ferritic and chromium–aluminium steels must not be stripped so early ; (2) transformer steels and 25%-Cr steels must cool slowly ; and

(3) the Cr–Mn, Cr–Mn–Mo, Cr–Ni, Cr–W–Mo, and Cr–W–V low alloy steels and the high-alloy tool steels are particularly sensitive to hot tears.—P. F.

PRODUCTION OF FERRO-ALLOYS

Ferro-Alloy Manufacture in Japan Today. S. Shioya. (*Tetsu to Hagane*, 1953, **39**, Apr., 437–448). [In Japanese]. The author reviews ferro-alloy manufacture in Japan. (11 references).—R. A. R.

Recent Developments in the Electric Smelting of Minerals: Importance of Cheap Hydro-Electric Power. A. G. Robiette. (*Iron Coal Trades Rev.*, 1953, **166**, June 5, 1279–1284). The author discusses the present applications of electric smelting and describes the main processes, the types of plant, and their operation in ferro-alloy and pig-iron production and in non-ferrous smelting. Possible trends are outlined, with particular reference to the development of British and Commonwealth raw materials and hydro-electric resources.—G. F.

On Sampling Ferro-Alloys. K. Swoboda. (*Radex Rundschau*, 1952, (5), Oct., 222–223). A concise outline is given of commercial methods of sample taking as used by buyers and producers of ferro-alloys.—E. C.

FOUNDRY PRACTICE

Outstanding Opportunities for the Foundry Industry. J. H. Smith. (*Amer. Foundryman*, 1953, **23**, June, 42–47). The author discusses some of the trends that he considers may revolutionize the foundry industry. These include shell moulding, high pressure moulding, and the development of nodular iron, low-sulphur grey iron, and the improved pearlitic malleable iron, as well as the application of quenching and tempering, and martempering to cast irons. The training of foundry engineers is also dealt with.—B. C. W.

Progress in Foundry Practice in the Second Half of 1952. P. A. Heller. (*Stahl u. Eisen*, 1953, **73**, June 18, 854–859 ; July 16, 985–987). The literature is reviewed. (80 references). R. A. R.

Operating Experiences with Hot-Blast Cupolas in Great Britain. F. C. Evans. (Inst. Brit. Foundrymen : *Foundry Trade J.*, 1953, **95**, July 16, 73–78 ; July 23, 113–117). Details are given of three hot-blast cupolas at present operating in Great Britain. The first produces malleable iron and uses a gas-fired Schack tubular recuperator to heat the blast to 425° C., although tests indicate that it would be possible to run the cupola on a completely recuperative cycle. The second consists of a Schack tubular convection recuperator coupled to a continuous tapping cupola producing cylinder iron ; the blast temperature is 500° C. The third, which produces iron for centrifugal castings, uses a Schack spiral radiation recuperator to give a blast temperature of between 400° C. and 500° C. The operation of the three cupolas is discussed and a critical assessment is made of their respective performances. Experiences with these cupolas have shown that the use of hot-blast gives a reduced coke consumption, a lower sulphur content in the metal, much lower silicon and manganese losses from the charge, increased tapping temperatures, and enables more steel scrap to be used in the charge. The foundry making centrifugal castings reports a decrease in scrapped castings and an almost complete cessation of dust emission.—B. C. W.

Another Hot-Blast Cupola Plant. (*Foundry Trade J.*, 1953, **95**, July 23, 119–122). A description is given of the conversion of two cupolas to hot-blast at Dartmouth Automobile Castings Ltd. The system is recuperative and delivers the blast at about 500° C. The cupolas have an internal diameter of 46 in. and melt at the rate of 10–11 tons/hr. Although the plant has only been operating for a short time the charge-coke consumption has fallen by 20%, the consumption of silicon briquettes by 70% and the limestone addition by 60%. There has been an appreciable reduction in the emission of dust and grit into the atmosphere.—B. C. W.

Norwegian Vanadium-Titanium Pig Iron. J. Sissener. (*Foundry Trade J.*, 1953, **95**, July 2, 5–6). Norwegian pig iron contains small amounts of vanadium and titanium such that on remelting a charge with about 40% of this iron the final castings contain about 0·2% V, and between 0·7% and 0·10 %Ti. The iron is high in carbon and low in phosphorus and sulphur. The advantages claimed include less shrinkage and porosity, reduction of wear in service, and higher strength.

The Use of the Basic Cupola for the Production of High Carbon Iron for the Manufacture of Spheroidal Graphite Cast-Iron Pipes. W. de Micheli. (*Fonderia Ital.*, 1953, **2**, July, 517–520). [In Italian]. The author examines the working of a basic cupola using a very basic slag with additions of fluxes. Construction and repairs of the basic lining are described as well as furnace operation, hourly production and charge. Tests show that although low-grade charge materials are used, the iron is of high quality. Some disadvantages of the basic cupola are outlined. —M. D. J. B.

Constructional and Operational Data on Basic Cupolas. C. Longaretti. (*Fonderia Ital.*, 1953, **2**, Aug., 545–554). [In Italian]. The author gives a comprehensive survey of basic cupola construction and operational techniques based on information gathered from current technical literature. (24 references).—M. D. J. B.

Note on the Production of Castings from Basic Cupola Iron. M. Noris. (*Fonderia Ital.*, 1953, **2**, July, 521–523). [In Italian]. The author shows how ordinary dolomite was used to line a basic cupola in place of more costly materials. Analyses and mechanical properties of the iron produced are given and the advantages of the basic cupola are discussed namely : The purity of the iron obtained even with low-grade charge materials, the low sulphur content, the better casting characteristics and the better mechanical properties. Costs are also examined.—M. D. J. B.

Basic Cupolas. A. M. Plešinger. (*Slévárenstvi*, 1953, **1**, (1–2), 33–37). [In Czech]. The chemical and metallurgical principles involved in using basic cupolas, particularly the removal of sulphur and phosphorus from cast iron, are discussed. Removal of both elements is incomplete but the metal is suitable for ingot moulds and as malleable cast-iron for numerous applications.—P. F.

Sidelights on a Study Tour of America. E. Hugo. (*Giesserei*, 1953, **40**, July 23, 374–384). The planning and organization of a team visiting the U.S.A. are outlined. Numerous foundry processes in the U.S.A. are compared with those in Germany, especial attention being paid to the question of productivity.—R. J. W.

Coke Saving by Constricting the Cupola Shaft. E. Offermann and H. Kühne. (*Met. u. Giesserei Techn.*, 1952, **2**, May, 148–149). Shaft constriction can only be used where the duration of melting or casting plays a subordinate part, because melting performance is reduced by about 10%. Slag control is important. A skin of slag will form on the tuyeres and this must be removed. Satisfactory results were obtained by altering the angle of the tuyeres.—L. J. L.

Cast Iron with Great Strength. O. Hoff. (*Dansk Tekn. Tidsskr.*, 1953, **77**, July, 187–191 ; Aug., 209–214). [In Danish]. Reasons for the re-emergence of cast iron as a first class constructional material are outlined. The iron–carbon equilibrium diagram is studied and inherent weaknesses due to the large flakes of uncombined graphite are pointed out. Attempts to improve quality are described. The advantages of keeping down the phosphorus content are discussed and details are given of the Meehanite method of manufacture. 'Synthetic' cast irons such as Ductite, made from steel scrap, coke carburized and inoculated with ferro-alloys.

Study on Chilled Rolls. N. Kamii and S. Kawamura. (*Tetsu to Hagane*, 1953, **39**, Feb., 135–140). [In Japanese]. Brittleness in chill-cast rolls from electric furnace steel is attributed to solution of graphite nuclei. To avoid this the temperature must be kept at 1450–1550° C. Furnace reactions are considered in two phases : (*a*) Oxidation, when charge adjustment and oxidation refining are important ; and (*b*) reduction when deoxidation and desulphurization are achieved, and control of ferrosilicon and depth of chill are important.

The High-Frequency Furnace in the Foundry. J. Mackievič and J. Zampach. (*Slévárenstvi*, 1953, **1**, (1–2), 9–16). [In Czech]. The advantages of high-frequency furnaces in foundry practice, the construction and principles underlying their operation, the choice of crucible material, and the manufacture of crucibles for melting steel for castings are discussed, and experience acquired in the making of permanent magnet steels, alloy steels, and non-ferrous metals are considered.

Experiments on Spherulite Formation in Cast Iron. J. Keverian, H. F. Taylor, and J. Wulff. (*Amer. Foundryman*, 1953, **23**, June, 85–91). In high-purity vacuum-melted iron–carbon, iron–carbon–silicon and nickel–carbon alloys, spherulitic graphite structures were obtained in the central section

of the ingots both with and without the addition of magnesium. It was observed that the contact angles against graphite of a commercial magnesium-treated cast-iron and a high-purity vacuum-melted iron–carbon alloy were both greater than for a normal untreated cast iron. This is attributed to an increase in the energy of the graphite-liquid interface brought about either by the reaction of surface-active elements with magnesium or by their desorption at low pressures. The increased interfacial energy delays the nucleation of graphite so that it finally forms in a supersaturated liquid and grows in a spherulitic manner.—B. C. W.

Investigations of the Crystallization of Nodular Graphite Iron. E. Scheil and L. Hütter. (*Arch. Eisenhüttenwesen*, 1953, **24**, May–June, 237–246). The rate of growth of spheroidal graphite is the same as that perpendicular to the plane of a flake. It must therefore be concluded that magnesium additions exert a restraining influence on the growth process. The graphite nodules are generally surrounded by a corona. In this there are not only concentration differences of mobile carbon atoms but also of the less mobile substituent atoms. It follows that the solidification has proceeded from the surface of the nodule to the outer limit of the corona. Whereas normal cast iron shows a pronounced eutectic arrest on the cooling curve, nodular graphite cast iron exhibits a more or less extensive temperature interval for the eutectic solidification. The structures produced by quenching magnesium-treated cast iron from temperatures above and in this interval show that the nodules are present at the start of solidification. There are also clear indications that nodular graphite can form indirectly from cementite and also directly from the melt. Indirect formation appears to be rare. It is most probable that nuclei form from the melt and the nodule then becomes very quickly surrounded by a corona. The further possibility that graphite nodules occur in the interior of primary dendrites from the γ-solid solution is considered unlikely. The possibility that the solidification interval is wholly or partly connected with a lowering of the eutectic freezing point is considered.—J. P.

Magnesium Additions to Malleable Cast Iron. V. Oliverius. (*Slévárenství*, 1953, **1**, (3), 60–63). [In Czech]. Results of preliminary experiments on the possibility of inoculating cast iron with magnesium compounds instead of with metallic magnesium are given. As a result of the diffusion of magnesium from magnesite, added to the liquid iron, transitional types of graphite, and some spheroidized graphite were found. Micrographs of all the types present are shown.

Pearlitic Malleable Castings. H. E. Steinhoff and L. Jenkins. (*Foundry*, 1953, **81**, July, 84–87). This is a description of the heat-treatment processes used by the Wagner Malleable Iron Co. for the production of pearlitic malleable castings weighing from ½ lb. to 11 lb. The castings are graphitized in a pusher type annealing furnace and then quenched in air in a specially designed cooling conveyor. This produces a fine-grained pearlitic microstructure with a uniform hardness of about 340 Brinell. The castings are subsequently tempered to remove residual stresses and to give the required hardness.—B. C. W.

Short Cycle Annealing for Malleable Iron. C. E. Rehder. (*Canad. Metals*, 1952, **15**, Oct., 70–72). This article gives a short description of 12 electric annealing ovens kept in continuous operation. The cycle used is 4 hr. heating up to 960° C.; 8 hr. holding ; cooling to 730° C.; holding for another 8 hr.; cooling in the furnace to below 650° C. ; and then remove. The castings are discoloured but no scale forms. Man-hours total 3·3 per ton of castings and electricity costs are $4·20 per ton. The annealed castings are not subject to galvanizing embrittlement.—J. C. B.

A New Method for Malleableizing of Cast Iron. M. Hofmann. (*Met. u. Giesserei Techn.*, 1953, **3**, May, 189–190). To economize in the use of fresh ore as a packing material for the annealing of iron castings, the author packed the castings in spent ore in cast pots 800 mm. in dia. and 900 mm. deep which were provided with 12 slits 100 mm. long and 15 mm. wide. Successful results were obtained after holding for 68–96 hr. at 1010–1040° C. The ore was used repeatedly, except for dust which was removed each time with a 4–5 mm. mesh screen.—R. A. R.

Research on the Annealing of White Cast Iron. I. Z. Ueda. (*Tetsu to Hagane*, 1953, **39**, Jan., 45–50). [In Japanese]. Malleable cast irons were subjected to short repeated heating cycles at various temperatures. Softening was promoted, as compared with single heating. At 870° C., the cementite scattered as globules, the iron tending to the high-strength pearlitic form. At higher temperatures, temper carbon increased and the iron became tougher. Even at temperatures such as 1050° C., the tendency to the coarse flaky graphite decomposition was much reduced. Generally, a tougher and stronger iron was produced.—K. E. J.

Production of Black-Heart Malleable Iron in a Cupola. J. Piaskowski and J. Raczka. (*Przeglad Odlewnictwa*, 1953, **3**, (6), 173–180). [In Polish]. Economic reasons for the change from the production from white-heart to black-heart malleable iron are presented. A description of the necessary equipment, iron composition, casting temperature, and heat-treatment for the production of castings from black-heart malleable iron is given.—V. G.

Construction and Operation of Coal Fired Air Furnaces. C. F. Semrau. (*Amer. Foundryman*, 1953, **24**, Aug., 34–39). Details are given of the construction and operation of three pulverized coal fired melting furnaces at the Illinois Malleable Iron Co., Chicago. The methods adopted to reduce wear of the refractory linings are discussed and the importance of correct charging is stressed. Correct charging also ensures that superheating and excessive oxidation does not occur and that the charge melts smoothly and uniformly.—B. C. W.

The Balanced Induction Crucible Furnace for Mains Frequency, with Rammed Crucible, Connected to a Three-Phase System. R. Lethen. (*Z. Metallkunde*, 1953, **44**, June, 267–272). A balanced single-phase circuit is described, and compared with the normal 3-phase circuits. Economies in cost and energy are claimed.—L. D. H.

The Use of Tilting Furnaces. Z. Eminger. (*Slévárenství*, 1953, **1**, (1–2), 37–46). [In Czech]. The designs of several small tilting arc furnaces for melting from a few pounds to half a ton of metal are described, and their use in the foundry, including the casting of high-speed steel tools, is discussed.

Research as It Affects the Customer. J. F. B. Jackson. (*Foundry Trade J.*, 1953, **95**, Aug. 13, 209–212). An account is given of the work of the British Steel Castings Research Association and the approach adopted by it to research and development in the foundry industry. Three of the Association's research projects, those on the mechanism of freezing, the burning-on of sand, and hot-tearing, are considered.

Critical Examination of Specifications for Foundry Sands. W. Götz. (*Fonderia Ital.*, 1953, **2**, June, 483–488 ; July, 524–530 ; Aug., 555–562). [In Italian]. The author examines the characteristics required of foundry sands in relation to different types of castings and studies the best type of apparatus to test these sands. (24 references).—M. D. J. B.

Ferrous Moulding. R. C. Mann. (*Proc. Inst. Australian Found.*, 1952, **5**, 97–100). A short practical account of ferrous moulding practice is presented.—B. G. B.

Servicing the Moulder. (*Anglo-American Council on Productivity, U.K. Section*, June, 1952.) This 18-page cyclostyled report gives information on what has actually been done by individual foundries in Great Britain to increase production by applying the recommendations of the Productivity Team which reported on its visit in 1950 to grey iron foundries in the U.S.A.—R. A. R.

Conveying Foundry Sands Pneumatically. C. J. Converse. (*Canad. Metals*, 1953, **16**, May 20, 30–32). The author describes in brief the Turbo-Drive used at the Warden King Ltd. plant at Montreal, to convey mixed core sand through a 4-in. pipe from the sand muller to any place required. This process is fully automatic and is controlled from a central panel.—J. C. B.

Dry Reclamation of Molding Sand Lowers Cost of Steel Castings. J. A. Cannon. (*Amer. Foundryman*, 1953, **23**, May, 68–73). The installation of a dry reclamation unit in a steel foundry reduced the amount of new sand used in eight months from 1040 tons to 240 tons. Reclaimed sand is used for facing and backing up, and the new sand for cores. The quality of the castings has not been impaired and there has been less scrap and less casting repairs than formerly, although part of this improvement must be due to better foundry technique.—B. C. W.

Wet Method for Sand Reclamation. C. E. Maddick. (*Canad. Metals*, 1953, **16**, May 20, 34–38). The author describes the sand reclamation plant at the foundry of Massey Harris Co., Ltd. It deals with 50–60 tons of cores daily and the sand is reclaimed by the Hydro-Blast wet sand method. The used moulding sand is washed free from clay

and its grain size established. Finally it passes through a drying tunnel. Its capacity is 3 tons/hr.—J. C. B.

Considerations on Drafting the New Standard DIN 52401 "Testing Foundry Sand". H. Jungbluth. (*Giesserei*, 1953, **40,** Aug. 20, 421–427).

Proposed German Standard "Testing Foundry Sand" DIN 52401. (*Giesserei*, 1953, **40,** Aug. 20, 428–433). The text of the proposed standard is given.—R. A. R.

Research on Core Sand Binders. I. H. Mikashima and H. Naridomi. (*Tetsu to Hagane*, 1953, **39,** Jan., 56–61). [In Japanese]. Green sand strength is improved by additions of rubber chloride, dextrin, and Novolack. Combination of these substances with linseed oil and resin also give excellent strength. The effects of additives on the permeability of the sand and the core are discussed.—K. E. J.

Testing Core-Sand Mixtures. H. Derlon and C. Rauh. (*Giesserei*, 1953, **40,** Aug. 6, 404–409). The lack of technical tests is first deplored and steps are suggested to remedy the position. The statistical use of experimental series is described, and illustrated with a frequency distribution curve of the breaking strength. The effect of various factors on the breaking strength is discussed separately. These include the effects of mixing, water content, binder content, drying temperature, cooling time, and naturally occurring fluctuations in the properties of sand.—R. J. W.

Chemical Testing of Core binders. R. Leo. (*Met. u. Giesserei Techn.*, 1952, **2,** June, 187–192). Having briefly surveyed the raw materials of commercial core binders, the author deals with sampling techniques, macroscopical and microscopical examination of the samples, and quantitative and qualitative analysis.—L. J. L.

General Observations on Core Binders. A. Lincke. (*Met. u. Giesserei Tech.*, 1952, **2,** June, 192–193). Core binders are classified into oils, emulsions, solidifying oils, dry binders synthetic resins, and cements, and the characteristics are briefly described.—R. A. R.

Patternmaking. J. R. Bray. (Inst. Brit. Found.: *Engineer Foundryman*, 1953, **18,** May, 83–89). Patternmaking for machine moulding in South African mechanized foundries is described.—L. D. H.

Patterns—Their Relation to Casting Procedure. T. H. Trevithick. (*Foundry*, 1952, **80,** Dec., 185–188; 1953, **81,** Jan., 191, 194, 196; Feb., 195–196, 199; Mar., 293–294, 296, 298; Apr., 217–218, 220; May, 243–250). Continuation of a series of articles (*see J. Iron Steel Inst.*, 1953, **174,** June, 174). The author discusses the production of patterns in the shortest possible time, and techniques which will facilitate work in the foundry. Sand moulding with special reference to facing sands and loams, the use and construction of sweeps, and shrinkage allowances are dealt with.—R. A. R.

Research in Pattern Coating Produces Quality Castings. C. J. Berg. (*Amer. Foundryman*, 1953, **23,** May, 80–86). The types of pattern coating in use are briefly reviewed and extensive data are presented on the properties of nine coatings including shellac and a crankcase sealer.—B. C. W.

Runners and Risers. E. Daybell, P. A. Russell, and R. W. Ruddle. (*Foundry Trade J.*, 1953, **94,** May 28, 601–609; June 11, 669–673). This is a report of a symposium organized by the Institute of British Foundrymen. In the first part a comprehensive account is given of gating and feeding methods as applied to steel castings. Top, bottom, and step gating is discussed together with the use of atmospheric-pressure heads, exothermic feeding powders, restricted-neck cores, and remote heat in producing satisfactory castings. The points discussed are illustrated both by photographs of actual castings and by diagrams showing the principles involved. Part II deals with iron castings. The author stresses the importance of preparing runners to avoid sand erosion, and the effect of pouring rate on the quality of the final castings. In Part III the principles of feeding and running non-ferrous castings are outlined.—B. C. W.

A High-Production Process for the Manufacture of Cast Iron Gutters. (*Machinery*, 1953, **83,** July 10, 57–58). Walter Macfarlane and Co. Ltd., a subsidiary of Federated Foundries Ltd., have developed a mechanized casting process for cast-iron gutters, which dispenses with sand moulds, boxes, and patterns. Details of this process, which has enabled output to be increased by about 200% are given.

New Cororeom Handles Jobbing Work Efficiently. J. E. Wolf. (*Foundry*. 1953, **81,** June, 118–119, 221). In an effort to overcome the bottleneck usually caused by coremaking in a jobbing foundry, a new cororeom has been built at the Mid-western Foundry Co., Coldwater, Michigan. The coreblowers and benches are placed on either side of a power belt conveyor which carries the cores to a continuous tower baking oven. Mixed sand is delivered from the rear to each bench so as not to interrupt core production.—B. C. W.

Special Stoving Processes. (*J. d'Informations Techniques des Industries de la Fonderie.*, 1952, Oct., 739). The use of infra-red and dielectric methods of heating, and of propane as a fuel for stoves is considered.—B. G. B.

Coremaking Speeded by the Use of Heated Corebox. W. M. Peterson. (*Foundry*, 1953, **81,** July, 106–107, 232). **Hot Boxes Bake Cores Without Use of Driers.** W. M. Peterson. (*Amer. Foundryman*, 1953, **23,** May, 87–89). By using thermostatically controlled electrically heated core boxes, cores may be blown and baked in one operation with a considerable saving in time. Baking times range from 10 to 90 sec. depending on core size, and, after drying in air for a few minutes, the cores are ready for use. The composition and preparation of the core sand is critical as the binders have to set in a few seconds and must not swell under heat or stick to the heated core boxes.—B. C. W.

How Fast Should a Mold Be Poured? H. W. Dietert. (*Foundry*, 1953, **81,** Aug., 205–206). The following formula is presented for calculating the pouring time required for grey iron castings $t = (A + T/B)\sqrt{w}$ where t is the pouring time in seconds, T the average metal thickness of the casting, W the weight of the casting in pounds, and A and B are two constants, the values of which for grey iron are $A = 0{\cdot}95$, $B = 0{\cdot}833$. Several graphical representations of the formula are given. Formulæ are also presented for calculating the effective sprue height and area of gate necessary to obtain the optimum pouring time.—B. C. W.

The Determination of the Rate of Mould Filling. K. Hess. (*Przeglad Odlewnictwa*, 1953, **3,** (6), 180–184). [In Polish]. Factors influencing the rate of filling a mould and formulæ proposed for determining pouring time are discussed. A nomogram for the determination of casting time based on the Sobolev formula is given.—V. G.

Studies High Pressure Molding. R. Heine and T. Barlow. (*Foundry*, 1953, **81,** Aug., 146, 148, 229). The high pressure moulding research carried out at the University of Wisconsin is reported. Sand is used, the grains of which are first coated with a carbon resin by hot mulling and then rendered tacky by the addition of a solvent. The sand flows easily under pressure and the casting tolerance is apparently limited only by the accuracy of the pattern equipment. As the sand is free from water it cannot dry out and it has a long life. The pressure, which is applied by squeezing, ranges from 80 to 600 lb./sq. in. The process is now in the pilot-plant stage.

Dietert Process for Precision Molds. H. W. Dietert. (*Amer. Foundryman*, 1953, **24,** July, 50–51). The Dietert process involves blowing a contoured core around a pattern to form half of a mould. The equipment required is a core blower, a pattern mounted on a blow plate, a contour drier, a core oven, and some means of clamping the half-moulds together during pouring. The oil binder used in the sand must be carefully selected, but otherwise the sand is normal core sand. The pattern fits into the drier and leaves a space of the required thickness into which the core sand is blown through holes round the outside edge of the pattern. After drying, the half-moulds are ready to be clamped together for pouring.

Dofasco Pours 99 tons of Steel. L. Frame. (*Canad. Metals*, 1952, **15,** Oct., 68–69). The author describes the preparation of the mould and cores and the casting of a 45-ton steel turbine rotor.—J. C. B.

Cast-Iron Pressure Pipe: History, Manufacture and Developments. R. V. Riley. (*Iron Coal Trades Rev.*, 1953, **167,** July 3, 15–22). The author outlines the history of cast-iron pipe manufacture and discusses in detail the development of the metal-spun and sand-spun techniques for producing large pipes centrifugally, with references to the patent literature. Other recent developments, including the possibilities of nodular iron for pipe manufacture, are also considered.—G. F.

Conventional Equipment Used in New Shell Moulding Process. (*Foundry*, 1953, **81,** July, 169–170). A description is given of a process for producing shell moulds using a core blower in conjunction with a contoured drier.—B. C. W.

Centrifugally Cast Stainless Steel Rings. C. V. Hotson. (*Canad. Metals*, 1952, **15,** Oct., 62–64). The advantages and disadvantages of centrifugal casting for high alloy steels

are discussed, and details are given of actual production control is obtained by radiographing all castings using cobalt$_{60}$ as the radioactive source. Care of moulds is very important to obtain the longest life from them, between 30 and 180 castings is the usual variation.—J. C. B.

Automatic Foundry Nears Reality. L. J. Bishop. (*Steel*, 1953, **133,** July 13, 98–100). The plans of a highly mechanized foundry are described. Starting point is the automatic shell moulding machine and subsequent movements and operations are largely automatic or mechanized. It requires 16 unskilled men to produce 50 tons of small castings every 8 hr. High quality work, metal economy and shop cleanliness are other features.—D. L. C. P.

Steel Foundry Plants "Down Under". T. H. Shartle. (*Foundry*, 1953, **81,** July, 226–228). Brief descriptions are given of several foundries in Australia and New Zealand.

New Brake Shoe Foundry Operating in California. (*Foundry*, 1953, **81,** June, 132–133). A description is given of the American Brake Co's new foundry at Pomona, California. The whole sand mixing system is entirely automatic and is push-button controlled by one man. There are three mould-producing lines each with a moulding unit at the head of a roller conveyor. After pouring the moulds are allowed to cool and then conveyed to the shake-out, where again one man controls the whole operation. Smoke from the two cupolas is passed through a cooling tower and then through an electrostatic precipitator before discharge to atmosphere.

Laying Out a Mechanized Shell Moulding Foundry. R. Olson. (*Foundry*, 1953, **81,** June, 108–112). The new shell moulding foundry at the Production Pattern and Foundry Co., Chicopee, Mass., makes and pours 3000 moulds/day and uses sand at the rate of 2000 lb./hr. The shell moulds, which are made on automatic machines, are fitted into the pouring boxes and backed up with gravel from an overhead hopper, before moving on a continuous conveyor to be filled. The conveyor doubles back to the shake-out station where the contents are dumped into a skip hoist bucket and taken to the second floor. Here the contents are fed through a chute on to a sloping double-decked vibrating screen, which sorts the castings from the broken shell moulds and backing-up gravel. The upper floor also houses the sand muller from which the sand–resin mixture is fed by gravity to the shell moulding machines on the lower floor.—B. C. W.

Mechanized Casting. J. Pascal. (*Mét. Constr. Mecan.*, 1953, **85,** June, 469–477). The mechanization of traditional moulding practices is discussed. The performance of various machines used for ramming the moulding sand, using compressed air, hydraulic or shaking principles, is described. An account of the operation of a machine operated by hydraulic power is given.—B. G. B.

Where Does Shell Moulding Fit in Your Parts Picture. H. S. Shroka. (*Iron Age*, 1953, **171,** June 18, 154–157). Experience with an automatic shell moulding machine which can produce 120 complete units per hour up to 12 × 18 in. in size are given. The expensive item is resin bonding which averages 5–7% by weight of the mix. Shell moulds have not proved conclusively economic as yet for general use but can be used where surface configuration between conventional and investment casting is required. Highest pouring temperature used has been 3100° F.—A. M. F.

Shell Moulding : New British Automatic Machine. (*Iron Steel*, 1953, **26,** Aug., 393–394). A description is given of the "Autoclino" automatic shell-moulding machine, designed for continuous production of half-shells at regular intervals. It consists essentially of an invertible support for the pattern plate, a sand-mixture hopper, and an infra-red-ray heater.

Considerations for Successful Use of Investment-Cast Type 410. D. von Ludwig. (*Metal Progress*, 1953, **63,** Apr., 84–87). The difficulties due to surface pitting in castings of a chromium steel (Cr 11·5–13·5%) produced by the investment casting method are discussed. The core structure is uniform and clean. A number of explanations of this pitting are considered, but no explanation of the phenomenon is considered satisfactory.—B. G. B.

Cutting Tools Cast by the Centrifugal Method. J. Doškář. (*Slévárenství*, 1953, **1,** (1–2), 28–30). [In Czech]. The development of centrifugally cast cutting and grinding tools, to replace forged high-speed steel tools, is discussed, and results obtained by experiments and in actual practice are given. Fine-grained low alloy steels of the ledeburitic eutectoid type, cast into specially developed ceramic moulds, had the same life, impact strength and other properties as the conventionally made tools.—P. F.

Shell Moulding *vs.* Conventional Sand Casting—Some Dramatic Cost Comparisons. (*Precision Met. Mold.*, 1953, **11,** July, 32–33). Details are given of cost saving achieved by redesigning small iron sand castings for the shell moulding process.—D. H.

Permanent Mold Grey-Iron Castings. E. C. Hoenicke. (*Mech. Engineering*, 1953, **75,** July, 549–550). Brief details are given of the process of producing grey iron castings in permanent moulds.—D. H.

Cutting Tools Cast by the Lost-Wax Method. T. Calinski. (*Przeglad Odlewnictwa*, 1953, **3,** (6), 184–188). [In Polish]. The production of cast cutting tools by the lost-wax process is outlined. The possibilities of further developments in precision casting are discussed.—V. G.

The Centrifugal Casting of Iron. A. Possenti. (*Fonderia Ital.*, 1953, **2,** June, 477–482). [In Italian]. The author reviews the classical methods of spinning horizontal castings in permanent moulds and describes a method which he developed for spinning cast iron in sand moulds.—M. D. J. B.

Follow Boards and Matchplates. P. Dwyer. (*Foundry*, 1953, **81,** Aug., 195–196, 199). The methods used in mounting patterns to ensure accurate matching are described and details are given of the procedure followed in making a set of pattern plates in which the mould was to be rammed horizontally but poured vertically.—B. C. W.

The Manufacture of a Machine Bed by the Cement-Sand Moulding Process Using a Frame Pattern. W. Goth. (*Giesserei*, 1953, **40,** July 23, 391–393). The manufacture of a machine bed, 14·8 m. long, 157 cm. wide and 45 cm. deep by the cement-sand molding process is described. The bed is made in two lengths 740 cm. long which are later joined together. The whole process of manufacture is described from the drawing and planning stage, through the making of the pattern and the moulds, to the lining of the moulds and the pouring.—R. J. W.

The Manufacture of a Cast-Steel Slag Trough by the Cement-sand Moulding process. K. Strupatis. (*Giesserei*, 1953, **40,** Aug. 20, 438–440). The manufacture of a 9-ton slag trough by the cement-sand moulding process is described. The first stage is the preparation of the pattern. The making of the cope and drag and the casting procedure are then described and illustrated. The economics of the cement-sand process compare favourably with other methods and much time is saved.—R. G. W.

The Moulding of a Difficult Centrifuge Base. H. Seifert. (*Giesserei*, 1953, **40,** July 9, 364–367). This article describes the manufacture of a complex casting in the shortest and most economical manner. This is effected by first making two skeleton pattern parts and then the patterns. The pattern making, the mould assembly, and the casting are described in detail. The advantages of wet cleaning methods are enumerated.—R. J. W.

Installs Modern Sand Handling System. (*Foundry*, 1953, **81,** Aug., 202–203). This is a description of the sand conveying system recently installed at the Riverside Foundry, Bettendorf, U.S.A. The system eliminates man-handling of either mould or core sand.—B. C. W.

How to Specify Conveyer Belting for Foundry Applications. R. H. Herrmann. (*Foundry*, 1953, **81,** Aug., 86–93, 238–241). The types of conveyer belting used in foundries for both low and high temperature service are discussed. The operation of conveyer belting is considered with reference to width of the belting, speed of movement, capacity of the belt, arrangement and spring of idlers and pulleys, and the power required to drive the belt.—B. C. W.

Foundry Practice at Fraser and Chalmers. A. W. Bartlett. (*Foundry Trade J.*, 1953, **95,** July 9, 51–52, 64). The foundry of the Frazer and Chalmers Engineering Works of the General Electric Co. Ltd., produces castings ranging from 30 tons to 5 lb. in weight. Details are given of the moulding practice employed for the larger castings and of the metal compositions used.—B. C. W.

Mechanization. C. R. Day. (*Proc. Inst. Australian Foundrymen*, 1952, **5,** 104–117). The mechanization of foundry operations is discussed with special reference to the smaller foundries in Australia.—B. G. B.

Mechanized Handling Plays Major Role in Cleaning Room. (*Canad. Metals*, 1952, **15,** Oct., 34–36). This is a brief

description of a modern conveyor system used in the foundry cleaning and annealing departments of Auto Specialities Mfg. Co. (Canada) Ltd., Windsor, Ontario.—J. C. B.

Cleaning Cast Steel Armour. E. F. Ross. (*Foundry*, 1953, **81,** Aug., 178, 180–181). To cope with the considerable cleaning required by cast tank turrets two new automatic blast machines have been installed at the Cast Armour Division of American Steel Foundries, East Chicago, Ind. These are 'wheel blast' machines with the wheels mounted in the ceiling of the cabinet with a turntable underneath to carry the castings.—B. C. W.

Ford Foundry Cleaning Room Features Planned Efficiency. V. F. Stine. (*Amer. Foundryman*, 1953, **23,** June, 76–78). A description is given of the casting cleaning room at the new Cleveland foundry of the Ford Motor Co., which handles cylinder blocks and heads, and various small engine parts.

New Snagging Machine Triples Guide Output. W. M. Fitzsimmons. (*Amer. Foundryman*, 1953, **23,** June, 56–57). A description is given of a new semi-automatic snagging machine for grinding valve guides, which has been designed and constructed by the International Harvester Co., Indianapolis. Output has been raised from a maximum of 1100 pieces/hr. with hand grinding to 3000/hr., and there has been a decrease in the percentage of rejects.—B. C. W.

Foundry Defects. G. Somigli. (*Fonderia Ital.*, 1953, **2,** June, 499–507; July, 520). [In Italian]. The author examines all types of foundry defects which occur in everyday practice. Defects are classified by their principal characteristics, thus providing a sound basis for comparative studies of all types.—M. D. J. B.

The Influence of Molding Materials on the Incidence of Hot Tearing. J. M. Middleton. (*Amer. Foundryman*, 1953, **23,** June, 67–74; **24,** July, 60–66). This is a report of an investigation into hot tearing in which the contraction of a horizontal bar and vertical runner was resisted at one end by a spring, and at the other by a test block of moulding material placed between the runner and a plate attached to the moulding box. When the contraction was opposed entirely by the spring with the runner rigidly held, hot tearing was found to occur at a temperature of about 20° C. above the solidus. This agrees with the theory of Bishop, Akerlind, and Pellini that hot tearing occurs through the last liquid films remaining between the dendrites. The likelihood of hot tearing was found to be increased by dry sand (as compared with green sand of the same density), increasing density of sand whether green or dry, increasing coarseness of the sand, and compacts containing organic binders. With the exception of those containing fireclay, the compacts with clay binders, only gave rise to small tears. Decreasing the casting temperature decreased the probability and extent of hot tears, and in castings restricted by compacts containing linseed oil, higher casting temperatures made the tears more severe.—B. C. W.

How to Avoid Rejects in Thin-Walled Castings. A. Kuntze. (*Met. u. Giesserei Techn.*, 1952, **2,** May, 168). Using cupola iron to manufacture cast iron bath tubs 3·5–4 mm. thick instead of Schürmann furnaces, gas cavities were found in many castings. The sulphur content in the Schürmann-type furnaces was 0·075%, in the cupola it averaged 0·12%. The cavities disappeared when coke containing only 0·8% sulphur was used. This and two other examples are described to demonstrate the ill effects of sulphur.—L. J. L.

Use of a Rotary Magnetic Field in the Casting of Metals. D. A. Shtanko. (*Zhurnal Tekhnicheskoi Fiziki*, 1933, **3,** 7, 1085–1090). The experiments described, which were made with zinc, aluminium, aluminium bronze and grey iron, indicated that: (1) Agitation of molten metal by a rotary magnetic field assists gas bubbles and non-metallic inclusions to come to the surface; (2) this agitation during cooling makes castings and ingots more homogeneous by breaking up the columnar crystals on the mould wall; and (3) the temperature of the metal is more uniform during cooling and thermal stresses in the casting are reduced.—R. A. R.

Internal Porosity and Inverse Segregation in White Cast Iron. W. B. Sobers. (*Foundry*, 1953, **81,** June, 128–131, 284–288). The solidification of steel and cast iron is discussed and the differences in behaviour between steel, white iron, and grey iron are illustrated in detail. The formation of porous spots in white cast iron is described and an explanation of the accompanying inverse segregation is given.

Cracks and Hot Tears in Steel Castings. J. B. Caine. (*Foundry*, 1953, **81,** June, 120–127, 289–297). This is a comprehensive review and discussion of the work carried out on hot tearing over the last 20 years. The effects on hot tearing of strain concentration, temperature gradients, chills, gates, risers, sand, temperature, and composition are all considered. The generally accepted stress theory of hot tearing is rejected in favour of the strain theory suggested by Bishop, Ackerlind, and Pellini. The author considers that the following points have been established: (1) Hot tearing is due to strain concentrations in the last remaining liquid films between the solid dendrites; (2) the temperature at which it occurs is very close to the solidus; (3) the contraction required to cause tearing is measured in thousandths of an inch; (4) the stress required is very low, certainly less than 50 lb./sq. in. and may be almost zero; and (5) hot tearing can occur within 1 min. after pouring or as much as 25 min. later.—B. C. W.

Faults in Castings and Their Causes. Part IV. (*Gjuteriet*, 1953, **43,** May, 81–89). [In Swedish]. A detailed analysis is made of the causes of surface defects in castings, such as rough surfaces, flash, strain, cuts, washes, burn-on and metal penetration. The last two are dealt with in detail.—G. G. K.

Stress Relief of Grey Iron. C. O. Burgess. (*Foundry*, 1953, **81,** Aug., 112–114; Sept., 128–131, 302–304). The main causes of internal stresses in castings are: (1) Differential cooling in a single section; (2) differential cooling between two or more sections; and (3) resistance of the sand to the contraction of the casting. Internal stresses may decrease the strength of the casting, give distortion during cooling or on subsequent machining, or even crack the casting. The stresses may be relieved by reheating the casting to allow plastic deformation to take place. Temperature is more important than time and little stress relief occurs below 750° F. (400° C.); temperature between 950° and 1050° F. (510° and 565° C.) are generally used. Most of the stress is relieved in the first hour.—B. C. W.

What the Fluidity Test Reveals about Grey Cast Iron. L. F. Porter and P. C. Rosenthal. (*Foundry*, 1953, **81,** Aug., 94–99, 245–249). The fluidity was determined with a spiral fed by a central sprue with an overflow basin to establish a constant flow; good reproducibility was obtained. A correlation has been established between pouring temperature, fluidity expressed in inches of spiral, and a composition factor (% C + $\frac{1}{4}$ Si% + $\frac{1}{2}$ P%). A chart is presented which enables any one of these to be determined if the other two are known. The effect of sulphur contents greater than 0·1% in decreasing fluidity was only observed when sufficient manganese was present to form MnS. The fluidity of grey cast iron increases with the carbon equivalent (i.e. C% + $\frac{1}{3}$ Si% + $\frac{1}{3}$ P%) up to about 4·55 and then drops rapidly. Oxidation or reduction of the melt did not significantly affect the fluidity.—B. C. W.

Maintenance in the Foundry. T. J. Glaza. (*Amer. Foundryman*, 1953, **24,** July, 40–44). Problems of maintaining foundry equipment are discussed. The author deals with motors and their drives, compressed air equipment, sand conveyers, mixers, and shake-out units.—B. C. W.

It's Harder to be Safe in Jobbing Shop Operations. E. Fry. (*Foundry*, 1953, **81,** June, 113, 277–280). The author discusses the difficulties in ensuring adequate safety precautions when many different jobs are being undertaken, and stresses that safety considerations should come first in planning any new order. The safety precautions that should be undertaken in different sections of a foundry are outlined.—B. C. W.

Positive Safety Programme Reduces Foundry Accidents. F. W. Shipley. (*Amer. Foundryman*, 1953, **23,** May, 74–77). The safety programme applied in the foundry of the Caterpillar Tractor Co. is described and it is shown how time lost by accidents may be substantially reduced.—B. C. W.

HEATING FURNACES AND SOAKING PITS

Notes on European Furnace Practice. M. H. Mawhinney. (*Indust. Heating*, 1953, **20,** July, 1315–1318). European reheating and heat-treating furnace design, practice, and the fuels used are briefly considered.—R. A. R.

High Production Rate in Automatic Gas Equipment Heating Heavy Chain Bars for Offsetting. C. S. Thomas. (*Indust. Heating*, 1953, **20,** July, 1276–1282). Equipment for the automatic local heating of small metal blanks, used in the construction of chains in mechanized shovels and similar heavy equipment is described. Natural gas is used, and the central portion of the blank is heated to 1250° F. For blanks $3\frac{1}{2} \times 9 \times \frac{5}{8}$ in. a heating rate of 300 blanks/hr. is obtained.—B. G. B.

Rotary Furnace Features Floating Hearth. R. E. Greenawalt. (*Indust. Heating*, 1953, **20,** July, 1320–1330). A description of a 49-ft. diameter rotary furnace for heating steel billets (9 ft. 6 in. long by 4 in. in dia.) from cold to 2400° F. at a rate of 20 tons/hr., is given. A special feature of the furnace is the design of the rotary hearth. This is made up of 20 steel segments each fitted to two wheels ; the segments are fitted together with clips.—B. G. B.

Economical Heating Furnace. S. I. Kutuzov. (*Stanki i Instrument*, 1953, (2), 36–37). [In Russian]. A simple furnace is described in which parts can be prepared for forging with an expenditure of 200–300 g. of liquid fuel per kilogram of charge.—S. K.

HEAT-TREATMENT AND HEAT-TREATMENT FURNACES

Heat Treatment of Steel. F. Bowman. (*Mines Mag.*, 1953, **43,** May, 23–24, 32). A brief survey, illustrated by the Fe-C phase diagram and a T.T.T. curve, reviews the objects and processes of normalizing, spheroidizing, sub-critical annealing, stress relieving, baking, annealing, quenching and tempering, austempering, marquenching, pack and gas carburizing, cyanide hardening, Chapmanizing, nitriding, tempering, and sub-zero treatment to prevent the retention of austenite.—K. E. J.

Heat-Treatment Furnace Developments. (*Metallurgia*, 1953, **47,** May, 247–262, 274). Recent installations, for ferrous and non-ferrous metals, are reviewed to show the progress in the design of heat-treatment plant. Details and illustrations of 42 pieces of heat-treating equipment are given, together with general information.—B. G. B.

Heat-Treatment Furnaces. A. J. Blackwell. (*Elect. Rev.*, 1953, **152,** May 22, 1149–1154). A brief description is given of electric heat-treatment furnaces of various types for hardening, tempering and nitriding, and the advantages of electrical heating in its metallurgical applications are indicated.—L. D. H.

The Problem of Metallic Heating Resistances for Electric Furnaces in Controlled Atmospheres. (*Usine Nouvelle*, 1953, **9,** Mar. 19, 49–53 ; Apr. 2, 23–25). Causes of failure in helical resistance elements are considered and attributed to too close winding locally, or too close contact with the refractory, thus causing local overheating. Optimum shapes are discussed in relation to the concept of equivalent specific surface load. The advantages of furnaces with variable power rather than on-off control are stressed and a method of compensating for the thermal inertia of a furnace is outlined.

The Heat-Treatment of Metal and Its Fire Hazards. R. W. Oxenbury. (*J. Chartered Insurance Inst.*, 1953, **50,** 315–344, Reprint). A detailed description is given of the principle operations used in the heat-treatment of metals ; these include normalizing, annealing, hardening, tempering, and case hardening. The risk of fire during these processes is considered.—B. G. B.

Heat-Treatment of Tool Steels. F. L. Darbyshire. (*E.S.C. News*, 1953, **7,** (1), 2–7). An illustrated description of the methods used and the practice of the heat-treating of tool steels is given. Five groups of tool steels are considered : High-speed, hot working, shock resisting, cold working, and plain carbon steels.—B. G. B.

Versatile Furnace Installation for Job Lot Heat-Treatment. (*Indust. Heating*, 1953, **20,** June, 1102–1106, 1166). By careful planning of the charges, a pit type of controlled atmosphere furnace is used 24 hr. a day for carburizing, hardening, and tempering. Long cycle treatments, such as carburizing, are run during the night shifts. An overhead monorail hoist system is utilized for all charging, discharging, and quenching operations. Floor space and equipment investments are kept to a minimum and a production rate of one ton of steel treated per day is maintained.—B. G. B.

Double-End Batch Furnaces Speed Heat Treatment of Small Parts. (*Iron Age*, 1953, **172,** July 2, 136–137). A heat-treatment furnace where careful materials handling, accurate control of heating cycle, and an efficient load pattern can be obtained is described. Charging and discharging of containers are done simultaneously from both ends of the furnace. Programme control of the heating cycle with a cam is used, and air at 1 lb./sq. in. from a compressor feeds the gas through a single valve automatic proportioning control.

Continuous Normalizing, Hardening, and Tempering at Kropp Forge Co. (*Indust. Heating*, 1953, **20,** July, 1264–1272). Three new integrated furnaces, direct fired with dual fuel burners, for the heat-treatment of a special type of forging which requires normalizing, hardening, and tempering to meet rigid specifications are described in detail. The furnaces have been used for heat-treating a variety of forgings and the cycles used for treating the special forgings are given.

Production Heat Treatment of Motorcycle Parts. (*Indust. Heating*, 1953, **20,** July, 1295–1300, 1382). The heat-treating facilities used at the Harley-Davidson Motor Co. in America for the treatment of a wide range of motorcycle parts are described.—B. G. B.

Gear Steels: Heat Treating Gives Them Life. J. Obrebski. (*Steel*, 1953, **133,** Aug. 31, 94–96). The problem of obtaining very tough and accurately dimensioned gears is considered. A study is made of the technique of carburizing and heat-treating alloy steel gears with minimum distortion. Flame and induction hardening of teeth are mentioned.—D. L. C. P.

UZSh-1 Machine for the Hardening of Gears. (*Stanki i Instrument*, 1953, (4), 39). [In Russian]. A brief description is given of an oxy-acetylene gear-hardening machine to deal with straight-toothed gears from 200 to 1500 mm. in dia. The machine is fully automatic and, with modification of burners, can be used for hardening a variety of parts.—S. K.

Improvement of Tool Heat-Treatment at the "Frezer" Works. S. D. Brik, A. D. Prokhorov and N. F. Fesechko. (*Stanki i Instrument*, 1952, (5), 20–22). [In Russian]. The extensive use of alkali hydroxide and salt baths in the heat-treatment of tool and high-speed steels at the Frezer works is described. For the sub-critical temperature hardening of low-alloy steel final preheating is carried out in fused sodium chloride at 850–870° C., followed by quenching in a mixture of 75% potassium hydroxide with 25% sodium hydroxide at 180–210° C. All the heat-treatment operations have been made continuous, resulting in a nine-fold saving of time. High-speed tool steels are tempered in sodium or potassium nitrate at 560° C., giving increased productivity and avoiding the need for chemical or mechanical cleaning.—S. K.

Automatic Heat-Treatment of Fasteners in Continuous Furnace with Duplex Quench Tank. F. C. Schaefer and R. L. Burdsall. (*Indust. Heating*, 1953, **20,** June, 1056–1064). The continuous heat-treatment operation used for the hardening of screws, nuts, bolts, and fasteners is described in detail. Sealing arrangements at each end of the furnaces permit the use of any type of atmosphere. The steels vary from low-carbon to medium-carbon and include some alloy grades. In order to develop the maximum physical properties by heat-treatment some require quenching in oil and others in water. A combination quench tank allows either water or oil quenching to be carried out.—B. G. B.

Gas Carburizing in Ordinary Furnaces with the Aid of a Muffle. J. Zbořil. (*Strojírenstvi*, 1953, **3,** 5, 360–365). [In Czech]. A cheap and simple method of carburizing by means of a butane-propane-air mixture in a muffle is described.

On the Carbon-Restoration of Steels. III. M. Okamoto and N. Shirai. (*Tetsu to Hagane*, 1953, **39,** Apr., 402–412). [In Japanese]. A solid carburizing agent containing 20% of dehydrated $K_4Fe(CN)_6$ showed better results than the normal material containing $BaCO_3$ in that it also acted as a nitriding agent, its effect was apparent at lower temperatures, and penetration was deep. Addition of 5% Fe_2O_3 gave improved results. With steels treated by oxidation, decarburization could be treated by this means. (14 references).—K. E. J.

Flame Hardening of Cast Iron. M. R. Scott. (*Amer. Foundryman*, 1953, **24,** July, 52–56). Flame hardening can be applied to a wide range of iron castings that require selected areas to be protected from wear. The oxy-acetylene flame is recommended for hardening as the atmosphere can be adjusted to be neutral or reducing. Methods of measuring surface hardness are reviewed and the scleroscope is suggested as the most satisfactory.—B. C. W.

Flame Hardening by Gas. (*Indust. Gas*, 1953, **16,** Aug., 342–347). Details are given of two Peddinghaus flame-hardening machines. Both machines use the oxygen/town-gas process of heating. One is a fully automatic high production unit, the other a small machine for the hardening of gear teeth. The hardening temperature is controlled by a Milliscope temperature controlling device, the working of which is described.—D. H.

Induction Heating Helps Produce Better Gears. L. G. Miller. (*Metal Progress*, 1953, **63,** June, 109–110, 179). The use of a 50-kW. electronic induction furnace for the heat-

treatment of gears is described. Chromium-molybdenum steel is normally employed for the gears.—B. G. B.

Induction Heat-Treatment Plant. (*Metallurgia*, 1953, **48**, July, 18–20). An extension to the Electric Furnace Co.'s works at Burton-on-Trent is described. It is devoted to research and development relating to induction heating and also provides facilities for heat-treatment for the engineering industries. The heat-treating of pins, shafts, and ring and wheel type components is considered.—B. G. B.

Selection of Frequency in High-Frequency Surface Hardening. A. E. Sluchocký. (*Strojírenství*, 1953, **3**, (5), 365–370). [In Czech]. Methods of selecting the optimum frequency for the induction hardening of parts of different dimensions are explained.—R. A. R.

Structures and Properties of Some Carbo-Nitrided Cases. K. B. Valentine. (*Metal Progress*, 1953, **63**, June, 97–103). The results of bending load tests, impact fatigue test, microhardness tests and microscopic examinations on test bars carbonitrided by four different practices, indicated a considerable difference in fatigue strength between the test bars carbonitrided by the various treatments. Quenching in oil from 1550° F. is preferred for high fatigue strength. Cyanide-hardened test bars have greater resistance to fatigue failure than carbonitrided bars.—B. G. B..

Precipitation of Nitrides and Precipitation Hardening of Mild Steel after Cold Deformation. Z. Wusatowski. (*Hutník*, (Poland), 1953, **20**, (8), 250–254). [In Polish]. The influence of the precipitation of nitrides on the mechanical properties of steel, ageing after cold plastic deformation, complex ageing, and blue brittleness, the properties of pure iron and single iron crystals, and the influence of hydrogen reduction on the properties of mild steel are discussed.—V. G.

Pressure Nitriding for Hardening Internal or External Surfaces. R. L. Chenault and G. E. Mohnkern. (*Metal Progress*, 1953, **63**, Apr., 97–105). In the process described, the parts to be nitrided are placed in a closed container together with a capsule of ammonia. Alternatively the container is connected with a cylinder of gaseous ammonia at 200 to 800 lb./sq. in. pressure. Furnace temperatures of 1000° F. are suitable, the time varying with the type of steel and the case required. Consumption of ammonia is about 5% that of conventional nitriding and no special furnace is required.—B. G. B.

Continuous Short-Cycle Anneal for Spheroidization of Cartridge-Case Steel. O. E. Cullen. (*Metal Progress*, 1953, **64**, July, 79–82). Owing to the severe forming operations encountered during the manufacture of steel cartridge cases an annealing treatment for 0·30% carbon steel is required to develop a suitable microstructure. Details are given of a furnace for the continuous heat-treating of cartridge case blanks at the rate of 17,500 lb./hr. with a total heating cycle of 19½ hr.—B. G. B.

The Continuous Annealing of Cold Rolled Low Carbon Steel Strip. K–H. Muhr and A. Pomp. (*Stahl u. Eisen*, 1953, **73**, July 2, 885–894). Seven cold-rolled low-carbon strip steels made by different refining methods were annealed at different temperatures, times, and cooling rates after various amounts of cold reduction. The commercial requirement for rapid annealing was borne in mind. The annealed strips were examined by tensile, Erichsen, and cupping tests, and metallographically and by X-ray diffraction. In comparison with pot-annealed materials, all continuously annealed specimens showed a higher yield point and tensile strength, but lower deformability and inferior deep drawing properties. The effect of varying the annealing procedure on the increase in tensile strength was investigated. The continuous annealing furnace offers advantages over pot-annealing when steel of high tensile strength, particularly high yield point, is required and for which superior deep drawing properties are not necessary. Strip annealed in a continuous furnace has the same strength properties as pot-annealed strip which has been given a small amount of rolling.—J. P.

Critical Comparison of Heat-Treating Plants in Cold Rolling Mills. E. Schauff. (*Stahl u. Eisen*, 1953, **73**, July 2, 895–902 : *Iron Steel Inst., Translation Series No.* 476, 1953). The required properties of low-carbon strip steel, the fundamental annealing problems and the conditions in annealing furnaces are discussed. A critical comparison of pot, roller-hearth, hood, and continuous annealing furnaces, and of their advantages and disadvantages from the metallurgical, economic and operational viewpoints is made.—J. P.

To What Extent Are Stresses Relieved at Temperatures of 200–300° C.? R. Gunnert. (*Ciencia y Tecn. Soldadura*, 1953, **3**, May–June). [In Spanish]. The author considers that heating in the range of 200° to 300° C. reduces the stresses in the steel and finds that the relationship between the stresses in the heated specimen and those in the specimen before heating is the same as the ratio of the elastic limit of the material at temperature and that of the material at room temperature.—R. S.

Copper and Sulphur on the Steel Surface. W. Gilde and G. Willing. (*Met. u. Giesserei Techn.*, 1952, **2**, June, 180–192). When annealing copper-rich steel in an oxidizing atmosphere, copper and sulphur enrichment occur on the steel surface. Red shortness was found to occur when the copper dissolving capacity of the oxide was less than the copper content of the steel. It is suggested that there may be on the surface of the liquid steel a film of copper sulphide and manganese sulphide, causing stress corrosion during rolling or forging.—L. J. L.

Heat Treatment Oils. A. L. H. Perry. (*Sci. Lubrication*, 1953, **5**, June, 13–19, 36–37). Functions and properties are described for oils used in the heat-treatment of steel, *i.e.*, the operations of conventional hardening, hot quenching (martempering), and tempering.—K. E. J.

FORGING, STAMPING, DRAWING, AND PRESSING

Present and Future Developments in Heavy Forging Practice: I—Handling and General Manipulation ; II—Heating Furnaces and Their Operation; III—Forging Tools and Processes; IV—Oxy-cutting as an Auxiliary Process. R. Benson. (*Iron Coal Trades Rev.*, 1953, **167**, July 31, 239–245 ; Aug. 7, 317–323 ; Aug. 14, 359–366 ; Aug. 21, 411–416 ; Aug. 28, 461–469). In Part I, methods of handling forgings and the introduction, extended use, and advantages of manipulators are considered. Possible future developments in handling methods are discussed. Furnaces for heating the stock are considered in Part 2, and the advantages of fully-metered, automatically-controlled furnaces fired with clean gas are discussed. The operation of fixed-hearth furnaces is outlined, and improved methods of charging and discharging are reviewed. In Part 3, descriptions are given of heavy steel-forging tools and of the processes in which they are used, including swaging, spreading, necking, upsetting, bending, twisting, and the manufacture of hollow forgings. Practical information on effecting long and local bends and on reducing distortion is given, and the various methods of holding and changing tools during hot-forging of large components are described. Part 4 deals with present-day applications of oxy-cutting in heavy forging practice, the latest techniques for the removal of surface defects, deseaming, trepanning, oxy-machining, trimming, and parting-off being outlined. Finally, possible developments of oxy-cutting are indicated.—G. F.

Baldwin Builds World's Largest Split Die Forging Press. (*Welding J.*, 1953, **32**, July, 622–624). A pull-down type press, capacity 11,000 tons, being constructed by the Baldwin-Lima-Hamilton Corp., is described and illustrated. It will have a piercing ram at the top and a knock-out ram at the bottom, and two horizontal side rams. The main pull-down power will be supplied by two 51-in. dia., 60-in. stroke, single acting cylinders of 5,500 tons each. The bolster area is 10 × 10 ft., and the maximum vertical opening is 12 ft.

The Manufacture of High-Duty Forged Pressure Vessels. J. E. Russell. (*Alloy Metals Rev.*, 1953, **8**, June, 2–8). Materials, methods of manufacture, and testing of forced high-duty pressure vessels are described.—V. G.

16″ Rotary Forge Tube Plant at the Clydesdale Works of Stewarts and Lloyds, Limited. (*Anvil*, 1953, (**2**), 12, 16–19). The sequence of operations at the rotary forge tube plant of Stewarts and Lloyds Ltd., Clydesdale, is outlined and descriptions are given of the ingot reheating furnace, hydraulic piercer, rotary elongator, forging mill, and sizing mill. The plant produces plain-end oil-line tube of 10¾–16 in. outside dia. and thickness ¼ in. min.—G. F.

New Method Speeds Calculations for Forging Dies. J. A. A. Gurgel. (*Iron Age*, 1953, **172**, July 2, 138–141). A graphical method for calculating profiles of upsetting dies and depicting the material flow in forging operations is presented. The method represents the volume of a solid as an area which is constructed from a simple square-law curve and a straight line. The examples given include one showing how the movement of material between two stages of upsetting can be predicted.

The Deformability of Low-Alloy Structural Steel at High Temperatures. S. I. Gubkin, V. G. Osipov, and A. N. Danil'chenko. (*Izvestiya Akademii Nauk S.S.S.R., Otdelenie Tekhnicheskikh Nauk*, 1953, (6), 910–917). [In Russian]. The resistance to deformation, plasticity, and the coefficient of friction of low-alloy structural steel were investigated. The plasticity diagram was constructed from three curves determining the plasticity under impact compression, and impact and static tension. On the basis of experimental results the following conclusions are drawn : (1) The optimum temperature for forging and rolling is between 900° and 1200°C. (2) The maximum plasticity at 1200° C. indicates the possibility of rolling with large reductions. (3) With increasing volume undergoing deformation, the resistance to deformation at 800° C. and above is diminished. (4) The plasticity also decreases with increase in volume. (5) The influence of velocity on the resistance to deformation is negligible. (6) The plasticity of small specimens increases with an increase of compression velocity and decreases with increasing stretching speed.—V. G.

Forming and Heat-Treating Spring Harrow Teeth at Mid-West Forging and Manufacturing Co. (*Indust. Heating*, 1953, **20,** June, 1068–1074). A continuous production line consisting of a heating furnace, forging machine and tempering furnace, for forging and heat-treating spring harrow teeth for harrowing and cultivating, is described in detail.—B. G. B.

Production of Deep Hollow Shapes in Steel. R. Vockenberger. (*Betrieb. u. Fertigung*, 1952, **6,** Aug.–Sept., 143–147). Methods of producing deep hollow shapes by hot forging or by hot or cold drawing processes, as well as methods of machining deep holes by drilling, boring or trepanning are reviewed.—H. R. M.

Internal Cracks in High-Speed Steels and the Results of Forging these Steels. P. Iglesias Varela. (*Inst. Hierro Acero*, 1953, **6,** Apr.–June, 133–137). [In Spanish]. The origin and harmful effects of internal cracks in high-speed steels are discussed. The author believes that they originate, not in the ingot, but in the latter stages of forging, and are related to the size and shape of the hammers used.—R. S.

Early Experiments in the Cold Extrusion of Steel. H. J. Pessl and H. H. Hauttmann. (*Metal Progress*, 1953, **64,** July, 97–102). The development in Germany of the method of cold extrusion of steel is described. The results of experiments carried out on the effect of different lubricants, the effect of phosphate, copper and zinc coatings on the ease of extrusion are considered. Phosphate coatings have the advantage that they can readily be removed after extrusion by dipping in hot caustic soda solution.—B. G. B.

New Test for Drawability of Sheet Steel. C. B. Buker and J. R. Speer. (*S.A.E. Transactions*, 1953, **61,** 469–477). An instrument called a Flex-Tester is described and its use to determine the drawability of steel sheets is discussed. With this instrument a corner of the sheet is bent through a given arc and the resistance of the material to the bending force causes a tongue, acting as a cantilever spring, to deflect; this deflection is recorded on a dial gauge in what are termed F units. To obtain comparable values of F a correction for sheet thickness is applied. The test is simple, convenient, and non-destructive. The F values can be used to show the changes in rate and degree of ageing in steel strip.—R. A. R.

Effect of Steelmaking Procedure on the Deep Drawing Properties of Sheet. F. Eisenkolb and T. Brüggemann. (*Stahl u. Eisen*, 1953, **73,** July 16, 967–970). Deep drawing tests on normalized sheet made from killed open-hearth and electric furnace melts have demonstrated the influence of refining rate on steel quality—the faster the refining, the better the steel. Carbon content at melt-down has an indirect influence on drawing properties ; for best results it should be above 0·3%. The lower deformability of killed electric steel may be explained by the higher oxide content of the steel due to poor degassing and to the fact that a white slag cannot be used when melting down to low carbon contents. The results obtained on deep drawing sheets from aluminium-killed basic-Bessemer steel were not as good as those of similar sheets in open-hearth quality. Sheets from open-hearth melts, deoxidized with aluminium plus titanium, had no tendency to grain growth under critical recrystallization conditions. They have also a small- or McQuaid-Ehn grain size. This suggests that these elements combine with oxygen and nitrogen and form inclusions which are insoluble in the steel.—J. P.

The Manufacture and Manipulation of Seamless Tubes: Messrs. Accles and Pollock Limited. (*Engineering*, 1953, **176,** Aug. 7, 161–165 ; Aug. 14, 193–195 ; Aug. 21, 225–227). A comprehensive description is given of the activities of Accles and Pollock, Ltd. The manufacture of straight tubes, the process of drawing and the choice of drawing methods are discussed.—M. D. J. B.

Technology of the Manufacture of Bars and Tubes by Cold-Drawing. B. Puchnar. (*Hutník* (Prague), 1953, **3,** (6), 126–129). [In Czech]. Relations are derived between the changes in the dimensions of tubes and rods associated with various degrees of cold reduction. Nomograms for a rapid determination of lengths and diameters are given.—P. F.

Reeling Developments in Modern Wire Mills. A. G. Arend. (*Wire Ind.*, 1953, **20,** July, 689–691). Reels are described in which the laying motion is under automatic electric control, and is capable of handling water-quenched rod up to 0·4 in. and hot reeled rod up to 1 in. in dia. in coil weights up to 660 lb.—J. G. W.

A Modern Five-Pass Back-Pull Wire Drawing Machine. (*Stahl u. Eisen*, 1953, **73,** July 2, 919–921). A machine made by Kilshammar Mekaniska Verkstad, Kristinehamn, Sweden, is described. The wire passes through the first die, over a driven sheave, an idler pulley and then through the second die, over a second driven sheave, an idler, through the third die, and over the third driven sheave. The wire then passes through the fourth die, once round a fourth sheave, over an idler, through a fifth die, and on to the final sheave. The first three sheaves are coaxial and are driven by a differential gearing. The fourth and fifth sheaves are also co-axial and driven by a differential. The speed regulation of the sheaves is completely automatic and drawing speed is high. When three passes only are required, the wire passes through the second, third, and fifth dies and the fourth and fifth sheaves are locked together by a pin. When four passes are required, the wire passes through the first, second, third, and fifth dies, the fourth and fifth sheaves being again locked. The machine needs no mechanical adjustments for sheave speed nor for regulation of back pull. It is provided with water cooling for sheaves and dies and it automatically stops if the wire breaks or if the water supply is interrupted. It has a low speed for threading the wire through the dies.—J. P.

Pathfinder—A New Multihole Machine. (*Draht, German ed.*, 1953, **4,** Feb., 57–59). Particulars are given of the 'Pathfinder,' a multi-hole, wire-drawing machine of the non-slip, straight-line type. Reference is made to the improvement of torsional properties and surface quality of high tensile rope and spring wire by the use of a very light final pass.—J. G. W.

Economic Take-Up and Wind-Off Machines. F. A. Ebert. (*Draht, German ed.*, 1953, **4,** Feb., 43–49). Various designs of take-up and wind-off appliances for wire and strip are illustrated and discussed.—J. G. W.

Mechanical Handling at the Wire Mills of John A. Roebling's Sons Corporation. J. W. Maisch. (*Wire and Wire Prod.*, 1953, **28,** June, 567–571). Methods of handling and transportation in the New Jersey wire works of John A. Roebling's Sons Corp. are outlined and illustrated.—J. G. W.

Packing of Wire and Wire Products. A. H. Andrews. (*Wire and Wire Prod.*, 1953, **28,** June, 572–575, 628, 629). Various methods of packaging, as recommended in the U.S. Dept. of Commerce manuals, are described.—J. G. W.

Methods of Supervising Production and Evaluating Production Data. K. Daeves. (*Draht, German ed.*, 1953, **4,** May, 167–173). Elementary statistical concepts are introduced, followed by an explanation of quality control. The principles are applied to production control in a wire mill.—J. G. W.

The Technical Development of Needle Manufacture. F. B. Schmetz and E.-G. Haase. (*Stahl u. Eisen*, 1953, **73,** July 2, 908–914). The development of sewing-needle making from hand to automatic machine production is described, particular attention being paid to modern methods of making sewing machine needles and to the standardization of the product.

Novel Safety Appliances in Wire Mills. E. Neveling. (*Draht*, German ed., 1953, **4,** Apr., 135–137). Safety appliances for wire drawing machines, which recently came into use in Germany, are described.—J. G. W.

Safety in Wire Drawing Operations. A. E. Asel. (*Wire and Wire Prod.*, 1953, **28,** Apr., 374–378, 421). The author outlines the causes of the more common accidents in wire mills and describes the safety measures taken at the Sheffield Steel Corp. plant in Kansas City, Missouri.—J. G. W.

A Note on the Performance of the "Increasing-Load Wire Abrasion Tester." F. Levi. (*Wire and Wire Prod.*, 1953, **28,** Apr., 359–361, 419). The author disputes claims made for the "Increased-Load Wire Abrasion Tester" for vinyl acetate enamelled wires, and shows by theoretical argument and reference to experiments that they are exaggerated.—J. G. W.

Theoretical and Practical Determination of the Best Shape of Wire-Drawing Dies. J. Höll. (*Hutník* (Prague), 1953, **3,** (6), 130–134). [In Czech].

B.I.S.R.A. Profiloscope. J. G. Wistreich. (*Research*, 1953, **6,** July, 252–257). The profiloscope is a simple, robust die inspection tool which makes possible rapid measurement of die angle (within $\pm$ 0·5°), and qualitative examination of the sizing portion of the die, and of the zone where the reduction taper joins the parallel. It can be used for rapid quality control of die profiles.—K. E. J.

ROLLING-MILL PRACTICE

A Modern Rolling Mill Drive. J. P. Huggard and S. A. G. Emms. (*G.E.C. J.*, 1952, **19,** Oct., 195–202). A description is given of a new 42½-in. cogging mill installed at the Redbourn works of Richard Thomas and Baldwin Ltd. The blooms produced are 5 in. square and larger, and the slabs 9 to 34 in. wide and 1¾ to 6 in. thick. They are rolled down from 3 ton or 5 ton ingots. Full details of the electrical equipment installed are given.—B. G. B.

Application and Rating of Mill-Type Motors in Steelworks. D. A. Wise. (*Iron Coal Trades Rev.*, 1953, **167,** Aug. 14, 347–351; Aug. 21, 423–427). The application and rating of mill-type motors for steelworks auxiliary drives are discussed, and continuous, short-time, and intermittent working conditions are described. The possibilities of avoiding breakdowns, excessive maintenance, and uneconomical applications, are considered. This might be achieved by classifying duty cycles to assist in drawing up specifications and by obtaining comprehensive motor data under operating conditions.—G. F.

The New Type "1000" Rolling Mill. I. A. Rewin. (*Engineering News* (Moscow), 1951, **31,** 49–55; *Met. u. Giesserei Techn.*, 1952, **2,** May, 158–163). This is a detailed description, illustrated by diagrams and a photograph, of a Russian cogging mill with a capacity of 1·5 million tons per year driven by a 6000–7000 h.p. motor. Ingots weighing from 2½ to 6 tons are rolled down to blooms with cross sections ranging from 150 × 150 to 350 × 350 mm. and to plate 75 to 200 mm. thick and 300 to 900 mm. wide.—L. J. L.

Roll Pass Design for Beams. D. A. Winton. (*J. Iron Steel Inst.*, 1954, **176,** Jan. 3-17). [This issue].

Rolling Mill is Tale of Two Cities. (*Steel*, 1953, **133,** Aug. 17, 120–123). The new facilities at Pittsburgh Steel Company's Allenport plant are described. Low-carbon rimming steel slabs pass through a triple-zone gas furnace, scale breaking stand, a reversing roughing mill (which reduces the 5 in. slabs to ¼ in. in five passes), another descaler and four 4-high finishing stands, to the coiler. Further processing can clean, trim and oil about 40,000 tons of 20 to 60-in. sheet, 0·060 to 0·188 in. thick per month.—D. L. C. P.

New Hot Strip Mill at Pittsburgh Steel. J. C. Peth and F. E. Fairman. (*Blast Furn. Steel Plant*, 1953, **41,** Aug., 926–938, 944). A description is given of a 66-in. semi-continuous hot strip mill with a rated capacity of 600,000 tons/year; it is designed to produce hot rolled strip from 20 to 60 in. wide, 0·060 to 0·188 in. thick with a maximum coil weight of 30,000 lb. Cold slabs are obtained from another works and are heated in one of two triple-fired reheating furnaces. Full details of the rolling equipment and electrical drives are also given.—B. G. B.

Firth-Vickers' New Stainless Steel Strip Plant: Developments at Shepcote Lane. (*Anvil*, 1953, **3,** (1), 4–9; *Engineering*, 1953, **176,** Sept. 11, 322–333; Sept. 18, 362–365). The new Shepcote Lane plant of Firth-Vickers Stainless Steels Ltd. comprises hot and cold rolling sections and other processing equipment for the continuous handling of steel strip up to about 39 in. wide. This article describes the layout of the plant and gives details of its components.—G. F.

The Temper Mill Drives at the Trostre Works of the Steel Company of Wales. J. P. Huggard and S. A. G. Emms. (*G.E.C. J.*, 1953, **20,** July, 151–160). Two 2-stand temper mills, used at the Trostre Works for skin passing of coiled strip preparatory to tinning, are the first in the country to operate at speeds of up to 4000 ft./min. All electrical plant and control gear were supplied by G.E.C. These are described in some detail, demonstrating the application of the cascade control exciter system in conjunction with Ward-Leonard control for preserving correct strip tension.—E. C.

Continuous Train for the Hot Rolling of Steel Strip. (*Mem. Soc. Ing. Civils France.*, 1952, **105,** July–Aug., 423–431). A description is given of the new USINOR works at Denain in France for the manufacture of steel strip. Ingots of 10–15 tons are used. They are brought from the steelworks and are reheated in Heurtey-Salem gas-fired furnaces. The slabbing capacity is 250 tons/hr. and the mill is expected to produce 700,000 tons of steel strip per year. The strip is not tinned.

The Stresses in the Reels of Cold Reduction Mills. R. B. Sims and J. G. Place. (*Brit. J. App. Phys.*, 1953, **4,** July, 213–216). An investigation of stress distribution in the reels of a cold reduction mill indicates that it is nearly axially symmetrical. By measurement of the tangential stress in a lap of the coil next to the reel, it has been confirmed that Inglis's theory of wire winding can be adapted to give a reasonable approximation to the stresses over the surface of a reel drum in the form of a thick-walled tube.—J. O. L.

MACHINERY FOR IRON AND STEEL PLANT

Testing and Repairing P.V.C. Conveyor Belting. (*Colliery Guardian*, 1953, **187,** July 2, 20–22). A plastic impregnated conveyer belting has been developed which is fire-resistant and impervious to water, grease, acid, and fungus. Details are given of a testing machine for this product which has been designed to simulate working conditions in a mine.—B. C. W.

Plants Gain Weight with Electronic Scales. H. Chandler. (*Steel*, 1953, **133,** Aug. 17, 110–113). Weighing machines, consisting of strain gauge assemblies operating electronic recorders are being used in America. Platform, track, crane, conveyor, and tank scales are possible. Accuracy is reported good. The economic capacity is over 20,000 lb., and the operating time is 4–6 sec. There are limitations due to temperature effects, overloads, and eccentric loads. Results can be indicated, or recorded on tape, tickets or ledger sheets.

Straightening of Plates. R. Hartl. (*Österr. Masch. Elektrowirtschaft*, 1952, **7,** Sept., 416–421). The general principles of design of roller levellers for straightening plates are discussed and several machines are described.—H. R. M.

Modern Methods of Planing and Sectioning Ingots. E. Blaupain. (*Anales de Mec. Elec.*, 1952, **29,** Sept.–Oct., 243–248). [In Spanish]. The advantages of planing are outlined. Planing machines are described and illustrated. Data on depths of cut are given. A machine for slicing ingots is described.—R. S.

LUBRICANTS AND LUBRICATION

Laboratory Evaluation of Lubricating Greases. E. G. Ellis. (*Sci. Lubrication*, 1953, **5,** Feb., 11–16; Mar., 13–16, 26; May, 18–23; July, 17–23). Some characteristics and methods of application of greases are surveyed. Greases are considered as homogeneous plastic, or elasto-plastic-viscous solids which are coherent structures during storage, dispensing, and use. Testing methods are described for apparent viscosity and flow characteristics. The development of grease specifications is surveyed. Miscellaneous tests of grease include drop-point testing for melting point, heat or pressure testing for oil bleeding from grease, tests for deleterious effects of water in emulsions, and tests for oxidation of grease. (12 references).

The New Standard Method for the Measurement of the Viscosity of Oils and Other Liquids in C.G.S. Units. (*J. Inst. Petroleum*, 1953, **39,** Apr., 237–239).

Handling, Storing and Dispensing Lubricants. (*Sci. Lubrication*, 1953, **5,** July, 12–16; Aug., 16–23).—K.E.J.

Spontaneous Ignition of Lubricating Oils. C. E. Frank, A. U. Blackham, and D. E. Swarts. (*Indust. Eng. Chem.*, 1953, **45,** Aug., 1753–1759). Information is given on the effects of the atomic structure, additives, and metal surfaces in the spontaneous ignition temperatures of lubricating oil.

Lubrication in Metal Working. A. L. H. Perry. (*Metallurgia*, 1953, **48,** July, 3–10). The types, nature, and capacities of the main lubricants used in metal working (chipless forming and cutting operations) are discussed. Reference is made to the testing and evaluation of lubricants.—B. G. B.

Basic Properties of Lubricating Greases. C. J. Boner. (*Machine Design*, 1953, **25,** May, 129–135). A brief account of the composition, structure, and properties of typical soap-

base and non-soap-base greases is given. The effects of water, solvents and chemicals, temperature range of operation, speeds, pressures, and structural changes in service, are considered.—J. R. P.

Safety Alarm Devices for Lubrication Systems. (*Sci. Lubrication*, 1953, **5**, June, 25–28). Descriptions are given of pressure alarms, flow indicators, and thermostats manufactured by Monitor Patent Safety Devices Ltd. for use on marine main and auxiliary engines, steam turbines, and rolling-mill plant.

WELDING AND FLAME-CUTTING

Cone Arc Welding. P. Patriarca and G. M. Slaughter. (*Welding J.*, 1953, **32**, July, 597–602). A new inert-gas shielded semi-automatic arc-welding process is described. The process utilizes standard welding equipment and is applicable to the reliable fabrication of the miniature tube-to-header type of heat exchangers. Experiments were conducted using small diameter, thin-walled stainless steel tubing with header sheets of sufficient thickness to ensure the production of consistently good welds. The effects of arc current and welding time were not ciritical. Holes pitched at twice the outside diameter of the tube were desirable to prevent the overlap of fusion zones.—U. E.

Welding of Hot-dipped Galvanized Steel: Special Problems Involved. T. J. Palmer. (*Iron Coal Trades Rev.*, 1953, **167**, Sept. 4, 533–537). Available methods for welding galvanized steel are compared. The main problems in fusion welding, namely, health hazards and loss of protection due to zinc volatilization, are considered and the advantages of bronze-welding, which largely overcomes these problems, are discussed.—G. F.

Stainless Steel Welding. F. Schultz. (S. African Inst. Welding: *Engineer and Foundryman*, 1953, **18**, July, 107–113). The metallurgical characteristics of corrosion-resisting steels are reviewed. The effects of weld decay and air hardening are pointed out. Commercial welding processes are discussed generally.—A. D. H.

Flush Welds Withstand Impact Better Than Reinforced Welds. C. E. Hartbower. (*Iron Age*, 1953, **171**, June 25, 136–139). American naval research experiments show that, contrary to general belief, weld reinforcement is not beneficial even though it provides a greater cross-section. Transition from ductile to brittle behaviour in reinforced welds occurs at appreciably higher temperatures (80° F.) than in finish-machined weldments. Explosion tests were used to get balanced loading on the ¾ in. mild steel plate used.—A. M. F.

Resistance Welding Applications in Aircraft Stainless Steels. D. O. Samuelson. (*Welding J.*, 1953, **32**, July, 603–611). The types of materials used for resistance welding stainless steels and their influence on the selection of equipment and processes are discussed. A number of welding machines are described and illustrated.—U. E.

Inspection Technique for Quality Welding. L. Gilbert and W. B. Bunn. (*Welding J.*, 1953, **32**, July, 614–619). Some of the modern non-destructive methods of testing welds are briefly discussed.—U. E.

Copper in Type 347 Weld Metal. R. P. Wentworth. (*Welding J.*, 1953, **32**, July, 347s–351s). The effect of copper in type 347 weld metal was investigated. Micro-studies were conducted on heat-treated samples. Results of the investigation indicated that the presence of copper in type 347 weld metal neither retarded the transformation of ferrite to sigma phase nor rendered it less brittle. At a high ferrite level copper seemed to increase the sigma embrittlement.

Mechanics of the Explosion Bulge Test. C. E. Hartbower. (*Welding J.*, 1953, **32**, July, 333s–341s). The explosion bulge test is not a full-scale test. The explosive is used only as an expedient for obtaining the large force necessary to develop a bulge in thick plate, and the test itself is primarily an evaluation of the crack initiation stage of weld failure. The equipment and experimental technique are described.—U. E.

Structural Failures in Welded Ships. (*Welding J.*, 1953, **32**, July, 342s–346s). The paper describes an investigation of the causes of structural failures in welded ships.—U. E.

Welding Sequences and Uses of Heat. F. H. Dill. (*Midwest Engineer*, 1953, **6**, July, 3, 11–13). The nature and extent of shrinkage of structures during welding is considered. In a 120-ft. steel bridge floor, for example, which contains 20 butt welds and 60 lines of plug welds, the shrinkage would be about 2½ in. Methods of welding structures so as to minimize excessive shrinkage and distortion are discussed.—B. G. B.

Notes on the Study of Welding Fluxes. G. M. Blanc and B. H. Deglon. (*Rev. Soudure*, 1952, **8**, (4), 233–238). The authors examine the literature on the reduction and solution of oxides, the fusion temperatures of fluxes, their density, viscosity, surface tension, capillarity, solidification, and chemical constituents. (43 references).—M. D. J. B.

MACHINING AND MACHINABILITY

Free Cutting Steel. N. H. Bacon. (*Rail Steel Topics*, 1953, **2**, (1) 31–39). The free-cutting mild steels containing 0·25% S which retain good impact and hot working properties are discussed. Machinability is further improved by 0·2% Pb and lead alone is used in higher carbon and alloy steels. A tool breakdown test and the Lozenhausen machinability test are described.—A. D. H.

Study of External Cylindrical Grinding. H. Optiz. (*Microtechnic*, 1953, **7**, (4), 162–170). By the use of dimensional analysis, formulæ are developed for peripheral forces, scratch depth, and wear resistance of grinding wheels. Plastic models of three-dimensional graphs representing the characteristic functions obtained are illustrated, and their method of use shown by worked examples.—L. D. H.

Some Remarks Regarding Wear in the Flanks of Carbide Cutting Tools. L. H. Hovenkamp and E. Van Emden. (*Microtechnic*, 1953, **7**, (3), 116–121). In investigating the cause of selective abrasion on the flank of carbide cutting tools, the authors described an experiment in which two pieces of the same cold rolled bar steel are cut with similar tools. The authors concluded that the chief contributory cause of selective wear was the work hardened surface of the outside layer of the work, caused by previous machining.

Contribution to the Study of the Resistance to Wear of Cutting Tools. M. F. Eugène. (*Microtechnic*, 1953, **7**, (3), 122–126). An apparatus is described for observing the disturbance caused when a stream of water impinges on two steel plates set at various angles to simulate tool edges. The disturbance in the water is observed by making uniform additions of Bakelite powder. By comparing the phenomena obtained with photomicrographs produced from actual cutting operations, conclusions are drawn relating to various types of tool wear.—L. D. H.

Original Method of Measuring the Intrinsic Resistance to Wear of Cutting Tools. M. F. Eugène. (*Microtechnic*, 1953, **7**, (3), 127–131). After defining specific work of tool abrasion in terms of frictional work of removal and weight of material removed, the author describes an apparatus with which the specific abrasion work of several tools of varying composition was determined as a function of the cutting temperature.

Contribution to the Determination of Edge Temperatures of Cutting Tools by a Method of Analogy. J. Moisseeff. (*Microtechnic*, 1953, **7**, (3), 132–133). The author discusses difficulties in applying E. Bickel's method of determining maximum cutting temperatures and their distribution on the cutting edge by the use of a harmonic function. An improved technique is suggested and discussed.—L. D. H.

Remarks in Connection with the Problem of the Two-Dimensional Thermal Flow in the Vicinity of a Tool Cutting Edge. E.Bickel. (*Microtechnic*, 1953, **7**, (3), 134–135). The two-dimensional nature of the thermal flow in the zone investigated is demonstrated, and the method of employing 'heat-electrical' analogy to determine the thermal flow is described.—L. D. H.

Processing of Boron Steels in the Shop. G. D. Rahrer. (*Metal Progress*, 1953, **63**, May, 85–89). The machining, carburizing, hot and cold forming, and welding properties of a wide range of boron steels manufactured in the U.S.A. are discussed. The factors affecting the performance of the steel during these operations are considered.—B. G. B.

Grinding and Lapping Stresses in Manganese Oil-Hardening Tool Steel. H. R. Letner and H. J. Snyder. (*Trans. Amer. Soc. Mech. Eng.*, 1953, **75**, July, 873–882). The biaxial stress distributions resulting from grinding and lapping annealed manganese oil-hardening tool steel (0·9% C, 1·38% Mn 0·45% C, 0·41% W) were determined by sectioning the stressed surface layers and following changes in curvature of the specimen by means of optical interferometry.—D. H.

CLEANING AND PICKLING

Processing Lines for Rolled Steel Strip. J. G. Frith. (*Anvil*, 1953, **2**, (12), 4–7). The author outlines the processes in the production of rolled steel strip and gives brief descriptions of continuous pickling, continuous cleaning, annealing, coating, shearing, and coil preparation lines. Methods of joining the ends of coils are also mentioned.—G. F.

Galvanic Removal of Scale, Burrs, Rust and Surface Polishing, and Galvanic Acid Galvanizing. R. Beck. (*Wire and Wire Prod.*, 1953, **28**, June, 582–583: *Draht, English ed.*, 1953, Mar., 42–43). The newly patented 'Dynamisator', employing an alternating-current process for cleaning wire from scale and rust, is briefly described. It is claimed that cleaning costs are reduced by 60%, and the risk of acid embrittlement is avoided.—J. G. W.

"Color" and Reflectance of Stainless Steels. F. K. Bloom. (*Metal Progress*, 1953, **63**, June, 67–72). The percentages of light reflected at different wave lengths by polished samples of a variety of grades and finishes of stainless steel were determined. The difference in appearance of two similarly polished surfaces is primarily due to their absolute reflectances which have been determined for a number of stainless steels. Methods of improving the apparent brightness of surfaces by various polishing techniques are considered.

Electrolytic Polishing of Special Steels and Alloys. (*Aciers Fins Spec. Franç.*, 1953, July, 32–37). The principles of the electrolytic polishing process, its industrial applications with particular reference to its use for special steels and alloys, and the properties of surfaces obtained by this process are described.—V. G.

Principles of Inside Polishing and Buffing. E. F. Doyle. (*Metal Finishing*, 1953, **51**, June, 97, 98, 102). General considerations affecting the use of cotton buffing wheels or felt bobs for polishing the inside of hollow articles are discussed very briefly.—J. P.

Deburrer Beats Hand Method. (*Steel*, 1953, **133**, July 20, 94). A Roto-Finish machine has been installed to clean up aluminium or stainless steel compressor rotor wheels for jet engines. Eight wheels are tumbled at a time with grinding chips, water and a special compound. Time per wheel has been cut from 2 hr. to 8 min. by this machine.—D. L. C. P.

Tank Castings Get Shot Blasted. E. F. Ross. (*Steel*, 1953, **133**, July 27, 106–107). The automatic cleaning equipment built to handle the big one-piece cast steel hulls for Patton tanks is described. Cabinets take work up to 26 ft. in dia. and subject it to blasting by steel wire to blasting by steel wire pellets.—D. L. C. P.

Brushes: Production Tools for Good Surface Finishes. R. O. Peterson. (*Iron Age*, 1953, **171**, Mar. 19, 134–137). The selection and use of power driven brushes for various finishing processes are discussed and the major characteristics and applications are tabulated. Brush flexibility permits controlled blending of surface irregularities. Surfaces with an initial finish of 24 to 35 microinches can be brushed to a finish of 4 to 7 microinches. Major advantage over grinding is the removal of surface imperfections without appreciably changing the shape or dimensions of a part.—A. M. F.

Disposal of Spent Sulfate Pickling Solutions. (*Ohio River Valley Water Sanitation Commission Pamphlet*, Oct., 1952). This 76-page booklet, prepared by the Steel Industry Action Committee of the above Commission, condenses the voluminous literature on the disposal of spent pickling liquor. Neutralizing treatments, and the recovery of copperas, ferrous sulphate monohydrate, iron oxide, ferric sulphate, and iron oxide, and ammonium sulphate are all dealt with. Brief particulars are also given of the manufacture of Ferron (a building material) from sludge from pickle liquor, the extraction of manganese concentrate from lean ore using ferrous sulphate, and the recovery of magnesia from dolomite using spent pickling liquor.—R. A. R.

Metal Cleaning Bibliographical Abstracts 1842–1951. J. C. Harris. (*Amer. Soc. Test. Mat. Spec. Tech. Publ. No.* 90-B, 1953). This 132-page handbook contains a comprehensive list of abstracts arranged in chronological order. At the end there are subject, author, specification, and patent indices.

The Influence of Flame-Cleaning on the Properties of Steels. H. Kemper and W. Pomaska. (*Schweissen u. Schnieden*, 1953, **5**, June, 201–209; July, 256–267). The effects of gases, dusts, and vapours, and the amount of rust encountered during flame-cleaning are discussed. The influence of temperature on the structure and strength of the steel under static stress and on ageing was investigated. A method has been developed for determining stresses in flame-cleaned material. The sample was cut into sections and each section was examined individually with strain gauges. The crystal structure was examined by X-rays; stresses were highest at right angles to the flame path. Tests were carried out on high-tensile steels to determine the effect of flame-cleaning on fatigue. The fatigue strength decreased slightly. Finally, corrosion tests were carried out. Flame-cleaning is an effective method of rust removal. Brief mention is made of a new method of protection in which flame-cleaning is combined with a thermochemical treatment.—U. E.

Machine for the Liquid-Polishing of Cylinders. E. A. Satel', A. I. Shilin, M. A. Elizavetin, A. I. Vostokov, and L. F. Ivanov. (*Stanki i Instrument*, 1952, (9), 26–27). [In Russian]. The design, operation, and performance of a machine for polishing cylinders by means of a stream of liquid containing a solid abrasive produced by compressed air are described. The liquid-abrasive mixture is produced by mechanical stirring in two tanks from which it is forced to the jet head by air at an effective pressure of 0·5–1 atm. supplied to the tanks. In the jet head a further air supply at 4–5 atm. effective pressure produces the abrasive stream. In polishing steel cylinders, best results for speed and surface quality were obtained with a mixture consisting of 64·6 kg. water, 33 kg. electro-corundum, 2 kg. soda and 0·46 kg. sodium nitride.

Polishing Surfaces up to 10th and 11th Class of Surface Quality. G. F. Kudasov and M. Ya. Dubova. (*Stanki i Instrument*, 1952, (9), 27–28). [In Russian]. The use of abrasive-impregnated flexible rubber discs for producing surface qualities of the '10th and 11th' class on steel is described, with special reference to the manufacture of bearings. Optimum abrasive grain size was found to depend on initial surface quality, further reduction of grain size gave no corresponding improvement in surface quality. Graphs of resultant surface quality against disc speed, time of polishing, abrasive grain size and bearing size, respectively, are given. Flexible discs, because of the high working pressure required, give good results only with very rigid polishing machines.—S. K.

PROTECTIVE COATINGS

Trends in Better Finishes for Automobiles. J. Parina, jun. (*Metal Progress*, 1953, **64**, July, 83–86). Methods in use and under development to prevent the corrosion of motor-car components are reviewed. These include electroplating techniques, an aluminium dipping process, and a number of organic type enamels and lacquers.—B. G. B.

Throwing Power of Plating Baths. G. Bianchi. (*Chim. e Indust.*, 1953, **35**, June, 414–420). [In Italian]. The throwing power of plating baths cannot be determined numerically with accuracy as it depends on geometric factors of shape and size, the dimension of the electrodes, the size of the bath, and the nature of the solution. The author discusses the Haring and Blum technique, which has up to now provided a theoretical and experimental basis for determining throwing power, and puts forward a new method which, he claims, gives good results. (16 references).—M. D. J. B.

Rapid Control of Electrodes for the Deposition of Metals—Influence of Fluorine in Zinc Sulphate Solutions. E. Bertorelle. (*Chim. e Indust.*, 1953, **35**, July, 484–486). [In Italian]. The method described is based on the close examination of the deposits which can be obtained on a cathode placed in a particular position which respect to the anode in a suitably constructed triangular electrolytic cell. Results are given which show the influence of fluorine in zinc sulphate solutions.

Correct Impregnation of Castings Prevents Leakage, Internal Corrosion, and Spotted or Blistered Finishes. W. N. Pratt. (*Metal Progress*, 1953, **63**, Apr., 88–92). Methods of impregnating metal castings are discussed. The properties of a number of materials used for impregnation are compared; these include sodium silicate, tung oils, and polyesters based on styrene. Proper impregnation of parts to be plated is shown to minimize subsequent failure of the plated film.

Finishing Army Ordnance Shells. F. L. Bonem. (*Products Finishing*, 1953, **17**, June, 72–78). The methods by which steel cartridge cases for the 105-mm. recoilless rifle are made at Servel, Inc., Evansville, Indiana, are described. After all

machining operations are completed, the cases are cleaned in alkali, pickled, phosphated, chromic-acid dipped, dried, and coated by dipping in a baking phenolic varnish.—J. P.

My Experience with Analytical Control of Electroplating Solutions. G. B. Hogaboom. (*Metal Finishing*, 1953, **51,** June, 93–96, 102). The author recounts some personal experiences leading to the development of analytical control methods for a number of plating solutions. No particular methods are described.—J. P.

Experimental Plating of Internal Engine Parts. G. W. Grupp. (*Metal Finishing*, 1953, **51,** July, 53–55). After tests on various single metal and alloy electrodeposits, it has been found that a tin–cadmium alloy, produced as consecutive coatings and alloyed by heating at 340–345° F., could be used to produce an easily and economically applied corrosion- and galling-resistant coating on bolts, nuts, crankshafts, cam tracks, gears, valves, and cylinder walls of aeroplane engines.

The Significance of Air Velocity in Ventilation Design. J. Baliff. (*Products Finishing*, 1953, **17,** June, 83–90, 96–110). Some of the aspects that must be considered in the planning of ventilator systems for plating tanks, spray booths, and grinding wheels, are discussed with reference to the air velocity necessary to capture any noxious particles and convey them along ducting.—J. P.

Electrochemical and Electrometallurgical Industries. H. D. C. Rapson. (*Reports on the Progress of Applied Chemistry*, 1952, **37,** 362–385). The major portion of this review of the literature deals with progress in electrodeposition and metal finishing industries. (281 references).—R. A. R.

Japanese Electroplating Practice. E. A. Blount. (*Plating*, 1953, **40,** May, 477–482, 487, 497). Current production methods in the Japanese plating industry are reviewed.—J. P.

What to Plate. A. G. Gray. (*Steel*, 1953, **133,** July 20, 84–88, 96). Substitutes for conventional nickel plating, such as copper–chromium, zinc, and white brass are considered. Many examples are given of the plating used on specific items, to economize in nickel during the present shortage. Some alternatives are giving interesting results.—D. L. C. P.

Anti-Corrosive Treatment and Embellishment by Means of Coatings. J. Hoekstra. (*Chemisch Weekblad*, 1953, **49,** Mar. 28, 213–219). [In Dutch]. The use of coatings for protection against corrosion and for improving appearance is discussed in general terms, and adhesion problems are dealt with in detail.—R. A. R.

Plating-Room Controls for Pollution Abatement. (*Ohio River Valley Water Sanitation Commission Pamphlet*, July, 1951). This 20-page booklet has been prepared by the Metal-Finishing Industry Action Committee of the above Commission. It makes, in a concise form, recommendations on plating room control, plating solution recovery systems, and the prevention of leaks and losses, many of which lead to economies, and all of which will reduce the pollution of drainage systems.—R. A. R.

Disposal of Plating Room Wastes. V—Treatment of Cyanide Waste Solutions by Ion Exchange. C. A. Walker and W. Zabban. (*Plating*, 1953, **40,** Mar., 269–278). Waste waters containing copper, zinc, and silver cyanides can be freed from metal and cyanide by passing them through a cation exchange resin and then through an anion exchange resin. The metal and cyanide may be recovered in more concentrated form by treating the resins with sodium hydroxide solution ; the cation exchanger is converted to the hydrogen form by treatment with hydrochloric acid.—J. P.

Resistance to Corrosion of Metallic Coatings as a Function of Layer Thickness and of the Conditions of Electrolytic Deposition. H. W. Dettner. (*Met. y Elec.*, 1953, **17,** May, 42–46). [In Spanish]. Tests carried out by the author on electrodeposited chromium coatings show that resistance to corrosion is a function of coating thickness and of the conditions during electrodeposition. It is thought that this is due to the modification of the face-centred or hexagonal chromium atoms. When playing it was seen that corrosion resistance was improved at 50° C. when the current was reduced. Below 50° C. a lower current decreased the resistance to corrosion.

Protection of Iron Against Corrosion by Galvanizing and Tinning. E. Diaz-Varela Ceano-Vivas. (*Inst. Hierro Acero*, 1953, **6,** Apr.-June, 85–102). [In Spanish]. This is a general explanation of galvanizing and tinning. Properties of zinc and tin coatings and the mechanism of protection against corrosion are described.—R. S.

Galvanizing Furnaces with Radiant and Convective Heating. H. Rückemesser. (*Draht*, 1953, **4,** Apr., 137–138). Two different types of Körner galvanizing pots are described.

Kinetics of Galvanizing. D. J. Blickwede. (*Trans. Amer. Inst. Min. Met. Eng.*, 1953, **197;** *J. Met.*, 1953, **5,** June, 807–808). From microscopical examination of sheet steel samples dipped into pure zinc at different temperatures and for different periods of time, the author establishes that the rate-determining process of the galvanizing reaction is not diffusion. No alternative theory can be put forward from the data obtained.—G. F.

"Why" as Applied to Cyanide Zinc Plating. T. J. Menzel. (*Plating*, 1953, **40,** Apr., 364, 365, 377). The causes of and remedies for dull, rough, thin or blistered cyanide zinc deposits are discussed.—J. P.

Notes on the Attack of Iron by Zinc. R. Haarmann. (*Metall*, 1953, **7,** June, 406–412). The author reviews problems arising in hot-dip galvanizing, under the headings of erosion, pitting, and grain-boundary attack of steel pots by molten zinc. Types are attack are shown by 20 photographs.

Formation of Pimples on the Surface of Galvanized Sheets. H.-J. Wiester and D. Horstmann. (*Stahl u. Eisen*, 1953, **73,** July 2, 902–906). The causes of pimple formation on the surface of hot galvanized sheets have been investigated by pickling away the zinc and by metallographic examination. Pimples can be produced by solid components in the zinc bath, surface defects on the sheet, and mechanical damage to the surface after annealing. The appearance of the pimples depends on the way they are formed. Pimples due to solids in the bath can be easily prevented by removing the solids, but those due to surface defects can be eliminated only by removing the surface layer, *e.g.*, by scaling and pickling. Pimple formation due to mechanical damage occurs only under special conditions.—J. P.

Comparison of the Electrolytic and Hot-Dip Processes for the Manufacture of Tinplate. W. R. Lewis. (*Métaux-Corrosion-Indust.*, 1953, **28,** Apr., 175–183). The electrolytic and hot-dip processes for the manufacture of tinplate are compared and the properties of the plate produced by each method are discussed. An attempt is made to compare the cost of each process. In the case of electrolytic tinplate with tin 0·8 microns thick and hot dip tinplate with tin 2 microns thick, the cost of the former is 88% of that of the latter.

Chemical Treatment for the Protection of Tinplate. E. S. Hedges. (*Métaux-Corrosion-Indust.*, 1953, **28,** Apr., 171–174). During the processing of certain foodstuffs while canning, the tinned coating is discoloured. Methods used to protect the tin are discussed. These include electrolytic anodic treatment (similar to that used for the protection of aluminium) and dipping in warm oxidizing solutions. Both methods give a protective oxide film which is structurally different from that normally produced on tin in air. The second method is now used during the manufacture of tinplate, usually immediately after the fusion of the deposit and before the final greasing.—B. G. B.

British Streamline Tin Plate Lines. (*Steel*, 1953, **133,** July 27, 84–86, 104). A U.S. contributions to Steel Co. of Wales plants are mentioned, and the tinplate line at the Trostre plant is described.—D. L. C. P.

Influence of Operating Variables on Composition of Electroplated Lead-Tin Alloys. A. H. DuRose and D. M. Hutchison. (*Plating*, 1953, **40,** May, 470–476, 497 ; June, 630–632). The influence of current density, lead/tin ratio, total metal content and concentration of addition agent on the composition of lead-tin alloys deposited from fluoborate solutions has been investigated. The results are presented by graphs. A coulometric method for the determination of the alloy composition was tested. It is offered as an aid to solution control, in particular for the control of addition agent concentration.

Tin-Nickel Alloy Plate. (*Products Finishing*, 1953, **17,** May, 42–48). Some development tests by the Metal and Thermit Corp., New York, on the tin–nickel alloy electrodeposition process developed by the Tin Research Institute are described. The excellent corrosion resistance of the deposits is stressed and the composition of the bath, equipment, operating methods and control are dealt with.—J. P.

Phosphate Coatings Benefit Metal Finishing and Working. A. G. Gray. (*Metal Progress*, 1953, **63,** Apr., 106–109). By the proper selection of phosphate solutions and conditions of

treatment, it is possible to produce phosphate coatings on iron, zinc, and aluminium. Examples of the treatment used are given.—B. G. B.

New Mill Turns Out Bigger Copper-Clad Sandwiches. (*Steel*, 1953, **133,** July 13, 110–115). The new plant of the Superior Steel Corp. for producing copper-clad steel strip is described. Output will be 80,000 tons/year of 15-in. strip. Assembled, the clad billet is 4⅞ in. thick, which is reduced by subsequent hot and cold rolling to 0·030 in. Provision is also made for producing stainless steel strip in the same line.

Investigations of the Amalgams of the Metals Manganese, Iron, Cobalt, Nickel and Copper. F. Lihl. (*Z. Metallkunde*, 1953, **44,** Apr., 160–166). The amalgams were formed by electrolysis in a mercury cathode. In the case of iron, saturated ferrous sulphate solution was used as electrolyte, and amalgams with up to 12% iron were obtained. Radiographic examination confirmed that the iron is present in the mercury as a suspension. Experiments are described to illustrate the properties of the amalgam.—L. D. H.

Increasing the Life of Pulveriser Hammers. (*Australasian Eng.*, 1953, Mar. 7, 72*a*–72*b*). **Pulveriser Hammer Life Increased by Hard Facing.** (*Chem. Eng. Min. Rev.*, 1953, **45,** Mar. 10, 220–221). Hammers measuring 8½ × 1½ × ½ in. used in a hammer mill for pulverizing hard minerals were hard-faced with Cobalide 1 and Cobalide 4 and their performances compared with those of alloy steels formerly used. Cobalide 1 is an iron–chromium–manganese cast alloy of 3·8% nominal carbon content. Cobalide 4 is a tubular welding rod containing granular tungsten carbide which produces a deposit containing 60% of this carbide. Important increases in life were obtained with both of these facings.

Use the Right Process for Coating Steel with Aluminium. S. L. Chase and K. R. Van Horn. (*Steel*, 1953, **133,** Aug. 3, 98–101, 128; Aug. 10, 138–142). Recent techniques for coating steel with aluminium are described; the applications characteristics of each method are given, with examples. The coating improves the corrosion and heat-resisting properties of steel. Heating above 900° F. produces a brittle compound layer of aluminium and iron. The hot-dip method is most commonly employed for commercial coating of steel sheets, strip, and wire. Additions of beryllium, copper, or silicon reduce the thickness of the alloy layer.—D. L. C. P.

Here's How to Graft Aluminium Skin to Steel. D. K. Hanink and A. L. Boegehold. (*S.A.E. J.*, 1953, **61,** Apr., 40–45). The Aldip process (patented by General Motor Corp.) for coating steel parts with aluminium is described. After preliminary cleaning by electrolytic caustic bath or acid pickle, the parts are preheated and fluxed in a ceramic-electrode salt bath furnace. The aluminium dip is carried out in an induction furnace. A subsequent diffusion heat-treatment eliminates spalling and cracking of the coat. Details of the coat thickness, time of immersion, and the composition and structure of the coat after various heat-treatments are described and illustrated for mild steel and a chromium–molybdenum steel.—P. M. C.

Mechanised Phosphating Plant. (*Indust. Finishing*, 1953, **5,** May, 728–730, 736). A test programme was carried out by George Ellison Ltd., to determine the best way of providing a rust-proof finish and paint bond for cast-iron components of electrical switchgear. Treatment with 'Jenolite' proved most effective, and details are given of the new plant which treats 100 units (average weight 28 lb.) per hour.—K. E. J.

Improving the Performance of Electro-Metallizing Machines. A. D. Renev. (*Stanki i Instrument*, 1952, No. 12, 30). [In Russian]. Adherence of zinc to the nozzle of the atomizer of an electric metallizing machine has been prevented by replacing the ordinary cylindrical atomizer with a conical one made of polished steel and chromium-plated.—S. K.

The Influence of Fuel Gas on the Spraying of Metal Powders, W. McDermott and R. Dickinson. (*Engineer*, 1953, **196.** July 3, 6–9). The principles involved in the spraying of powdered metals are outlined; they indicate that almost any combustible gas may be used as a source of heat to melt the powder particles. The use of acetylene, methane, propane, butane, natural gas, coal gas, enriched coal gas, and enriched propane for metal spraying is discussed, and the chemical reactions in the flames are described.—M. D. J. B.

Prepainted Steel Strip for Production Forming. K. Rose. (*Mat. Methods*, 1953, **37,** Mar., 158, 160, 162). Brief details are given of a continuous strip enamelling plant, in which mild steel strip of 18 to 20 gauge and up to 18 in. wide is coated at the rate of 12 ft./min. The process comprises alkali cleaning and degreasing, phosphating, chromic acid dip, drying, enamel dip, and final baking. The coated strip can be roll-formed, sheared, punched, and riveted without damage to the coat.—P. M. C.

Assessing the Cost of Losses in a Vitreous-Enamelling Shop. C. Lobley. (*Foundry Trade J.*, 1953, **95,** July 2, 27–29). A description is given of the budget control and standard cost system as applied to the operation of an enamelling shop in a large gas-stove foundry.—B. C. W.

New Methods Pay off for High Temperature Ceramic Coating. (*Steel*, 1953, **132,** June 22, 88–90). The first plant designed and built to apply a ceramic coating to metal parts is described. Coatings about 0·001 in. thick are fused to the metal at 1800° F. The coating doubles the life of components subjected to aircraft engine exhaust flames, and many applications are envisaged.—D. L. C. P.

Evolution of Vitreous-Enamel Formulae. A. W. Murdoch. (Inst. Vitreous Enamellers: *Foundry Trade J.*, 1953, **94,** Apr. 2, 389–392; May 7, 531–536).

Lead Cyanamide. R. Delmas. (*Mét. Constr. Mécan.*, 1953, **85,** June, 497–501). Lead cyanamide is very effective as a pigment for anticorrosive paints. The results of a series of laboratory and field tests with paint containing this pigment are given. The paint film is hard, adhesive, and elastic, and the pigment should be of great value in paints for the protection of metals against corrosion.—B. G. B.

Paint Coating Thickness Meters. R. Quarendon. (*Engineer*, 1953, **196,** July 31, 130–133; Aug. 7, 162–166). Meters for measuring the thickness of paint coatings, are described. Coatings on magnetic, and non-magnetic, conducting, and non-conducting bases can be measured. The design, method of use, and limitations of the meters are described.—M. D. J. B.

Dynamic Painting in Steel Plants. J. K. Seyler. (*Iron Steel Eng.*, 1953, **30,** June, 71–73). The author discusses the importance of colour schemes in industrial plants and suggests that production depends greatly on cheerful surroundings. It is claimed that physical comfort or nervous tension can depend on colour; working conditions in over-heated places are improved by using 'cool' paints.—M. D. J. B.

POWDER METALLURGY

The Effect of Infiltration on Physical Properties of Sinterings. G. Stern. (*Precision Met. Mold.*, 1953, **11,** June, 92–102). The theory, practice and economic factors are considered in the category of ferrous skeletons and copper base infiltrants. The variables affecting infiltration, such as composition of the skeleton and infiltrant, time and temperature of infiltration, and heat-treatment, are dealt with. Details are given of the physical properties of various skeleton and infiltrant compositions.—D. H.

Sintered Steel Bushings Extend Life of Roller Chain. L. H. Whitney and R. Talmage. (*Iron Age*, 1953, **171,** June 25, 125–127). A roller chain with sintered steel bushings has been developed for use where standard chain is not or cannot be lubricated properly. Resistance to elastic and plastic deformation is less but bearing pressure is less and high particle hardness resists wear. Bushings of 12% porosity are used of a material containing about 5% Cu, 0·75% C, and the balance iron.—A. M. F.

The Laws Governing the Shrinkage of Cermet Briquettes During Sintering I. M. Fedorchenko. (*Izvestiya Akademii Nauk S.S.S.R., Otdelenie Tekhnicheskikh Nauk*, 1953, (3), 393–406). [In Russian]. The influence of variations in the specific surface of powders on the shrinkage during sintering was investigated and an attempt is made to relate the shrinkage process to the surface diffusion of atoms. Experiments were made with iron, nickel, and copper powders.

Test Methods and Devices for Sintered Iron Rotating Bands J. D. Dale. (*Amer. Soc. Test. Mat. Spec. Tech. Publ. No.* 140, *Symposium on Testing Metal Powders and Metal Powder Products*, Mar. 5, 1952, 3–14). The methods of testing sintered iron rings used on artillery shells in place of the usual copper driving bands are described. Two methods for the determination of minimum tensile strength and elongation are reviewed and compared with tests used in Germany during the war (1939–45).—B. G. B.

Quality Control of Metal Powder Gears. W. A. Hinkle. (*Amer. Soc. Test. Mat., Spec. Tech. Publ. No.* 140, *Symposium on Testing Metal Powders and Metal Powder Products*, Mar. 5, 1952, 15–23). The production of gears from an iron–copper or iron-graphite mixture, sintered and impregnated with a copper alloy, which are used in washing machines is discussed. The method is competitive with conventional methods of gear cutting.—B. G. B.

Porous Stainless Steel Compacts for Transpiration Cooling. F. V. Lenel and O. W. Reen. (*Amer. Soc. Test. Mat., Spec. Tech. Publ. No.* 140, *Symposium on Testing Metal Powders and Metal Powder Products*, Mar. 5, 1952, 24–42). The production of porous stainless steel blades, for use in gas turbines, which can be cooled by forcing a cooling medium through the blades while in use, is discussed. The strength of a number of austenitic materials was measured as a function of permeability at room temperature and at 800° and 1110° F.—B. G. B.

Methods of Testing Cemented Carbide Compositions. A. D. Stevens and J. C. Redmond. (*Amer. Soc. Test. Mat., Spec. Tech. Publ. No.* 140, *Symposium on Testing Metal Powders and Metal Powder Products*, Mar. 5, 1952, 43–53). The four test methods often used by manufacturers and consumers are hardness, specific gravity, X-ray diffraction, and metallurgical. Details of these methods are given.—B. G. B.

Metal Powder Size Distribution with the Roller Air Analyser. P. S. Roller. (*Amer. Soc. Test. Mat., Spec. Tech. Publ. No.* 140, *Symposium on Testing Metal Powders and Metal Powder Products*, Mar. 5, 1952, 54–67). The method of analysis described is based on the qualitative separation of size fractions in a stream of air. The apparent size of irregularly shaped particles is found to be qualitatively related to the diameter of a sphere separated at the same air velocity. The use of the apparatus for size analysis of metal powders is described.—B. G. B.

Metal Powder Particle Size Determination. R. P. Seelig. (*Amer. Soc. Test. Mat., Spec. Tech. Publ. No.* 140, *Symposium on Testing Metal Powders and Metal Powder Products*, Mar. 5, 1952, 68–74). A survey is made of the most important methods for particle size measurement. A comparison is made of the various types of apparatus used in respect of the particle size range covered, operating skill required, initial cost, and the time required for the determination.—B. G. B.

Some Experiences in Specific Surface Measurement of Metal Powders by Low-Temperatures Gas Adsorption. J. B. Haertlein and J. F. Sachse. (*Amer. Soc. Test. Mat., Spec. Tech. Publ. No.* 140, *Symposium on Testing Metal Powders and Metal Powder Products*, Mar. 5, 1952, 75–87). After reviewing the development of the Brunauer-Emmett-Teller and the Harkins-Jura methods, the authors describe their experiences in the design and operation of the low-temperature gas adsorption apparatus. A report is made of work done on various methods of particle size analysis on metal powders, including iron.—B. G. B.

PROPERTIES AND TESTS

New Ideas in the Study of Mechanical Properties of Solids. F. Gatto. (*Alluminio*, 1953, **22**, Mar., 137–147). [In Italian]. The author draws attention to the tendency today of substituting new parameters, more generally applicable to the mechanical properties of materials, for the classical characteristics of tensile strength, structure, and impact. These parameters, which define correlations between different conditions in the material (*e.g.*, correlation between tensile strength and hardness), are examined. (33 references).

Relationship Between the Mechanical Properties of Structural Steels. W. Moszynski. (*Hutnik*, 1953, **20**, (7), 218–229). [In Polish]. Methods for the statistical analysis of the interdependence of any two mechanical properties of metals are outlined. Statistical analysis was made of the relation between elongation and strength and between reduction in area and elongation for some carbon structural steels and the results are discussed.—V. G.

Brittle Fracture and the Notch-Impact Test. A. Taraldsen. (*Tekn. Ukeblad*, 1953, **100**, June 25, 557–558). [In Norwegian]. The mechanism of brittle fracture and plastic deformation is explained using a simple diagram. Materials which under normal conditions may exhibit similar characteristics can vary markedly when working conditions are unfavourable. Suitable test conditions can be simulated by a combination of low temperatures, rapid deformation, or unfavourable multi-axial stresses.—G. G. K.

The Significance of the Izod Test with Regard to Gear Design and Performance. J. E. Russell and W. T. Chesters. (*Engineering*, 1953, **176**, Aug. 7, 166–169). An investigation of the reaction of a gear to shock loading is reported. The most important design variable influencing the impact value is the ratio of the bending moment to the shear stress across the section of the specimen. The authors find that there is little point in requiring gear material to have an Izod value in excess of 5 ft. lb. as far as shock loading conditions are concerned. For high-duty gears 10 ft. lb. may be required.

Structural Failure and What We Learn from It. R. Weck. (*Society Engineers Trans.*), 1953, **44**, Apr.–June, 47–63). The author classifies failure in metal structures into six basic types : Static overload, brittle fracture of a ductile material, fatigue, corrosion, creep, and instability. The first four types are considered in detail. Several examples of failure by these four processes are given, the mechanism of failure is discussed, and possible methods of reducing the failure are suggested.

Variations in the Internal Energy of Metals Caused by Work Hardening. F. Eugène. (*Compt. Rend.*, 1953, **236**, May 27, 2071–2073). The speed of impact of a Ruelle-type ram falling on cylindrical test pieces of lead, mild steel, and copper is measured by a strobocinematographic method, while the sensible heat after impact is determined by means of sensitive thermocouples. After correcting for heat losses, the internal energy due to work hardening is very small (0·011 cal./g. for steel).—A. G.

Statistical Study of the Change in Impact Strength as a Function of Temperature in Mild and Extra Mild Steels. J. Ulmo, F. Bastenaire, and R. Borione. (*Compt. Rend.*, 1953, **237**, July 6, 59–62). A study has been made of the temperature/impact-strength relationship over the temperature range $-100°$ to $+50°$C. Owing to the dispersion unavoidable with this phenomenon, statistical methods were employed. The results suggest that, for a given specimen, the energy of rupture changes sharply over a narrow temperature range.—A. G.

Statistical Analysis of Behavior in the Transition Temperature Zone. R. W. Vanderbeck, H. D. Wilde, R. W. Lindsay, and C. Daniel. (*Welding J.*, 1953, **32**, July, 325s–332s). A detailed analysis is made of the behaviour of keyhole Charpy specimens in the ductile–brittle transition zone. The relationship representing the percentage of brittle breaks at each temperature coincided, within limits of error, with a cumulative frequency distribution curve, which becomes a straight line when plotted on arithmetic probability paper. Examples are given which indicate how accurate the estimates of transition temperature and range may be when different numbers of tests are performed, and when they are distributed in different patterns.—U. E.

Plastic Deformation of Iron Between 300° and 77·2° K. D. F. Gibbons. (*Trans. Amer. Inst. Min. Met. Eng.*, 1953, **197** ; J. Met., 1953, **5**, Sept., 1245–1250). The author describes experiments undertaken on the mechanism of plastic deformation of iron between room temperature and 77·2° K. and to contribute to knowledge of the low-temperature brittleness phenomenon occurring in tensile and impact tests. The tensile-testing apparatus used with two grades of iron, containing 0·0034 and 0·021% of oxygen respectively, is described and the results obtained are discussed.—G. F.

On the Validity of Assumptions Made in Theories of Plastic Flow for Metals. J. Marin and L. W. Hu. (*Trans. Amer. Soc. Mech. Eng.*, 1953, **75**, Aug., 1181–1190). Results are reported of a series of special biaxial stress tests made to check the validity of various assumptions used in theories of plasticity. Tensile biaxial stresses were introduced into a tubular specimen of a hot-rolled aluminium alloy by the application of an internal pressure and axial tension. A test to determine the validity of the distortion-energy criterion used in formulating the plastic stress/strain relations by the flow method showed that the results did not support this assumption.—D. H.

Stress Formation and the Mechanism of Primary Plastic Flow in Mild Steel. Z. Wusatowski. (*Hutnik*, 1953, **20**, (6), 191–194). [In Polish]. The mechanism of stress formation in grains and in the intergranular network, initial plastic deformation in the cold state, and the influence of the intercrystalline material on deformation beyond the plastic limit of a mild steel are discussed.—V. G.

Preliminary Considerations for the Study of the Plastic Field. R. Zingale. (*Metal. Ital.*, 1953, **45**, July, 239–241). [In Italian]. After considering the problem of plastic deforma-

tion, the author discusses a hydrodynamic analogy, investigates photoelasticity as a method of investigation, and lastly, examines the analytical discontinuity of the functions which define this problem.—M. D. J. B.

The Nature of Plastic Failure of Metals. V. A. Pavlov. (*Doklady Akademii Nauk S.S.S.R.*, 1953, **91,** (2), 253–255). [In Russian]. An attempt was made to study the changes in properties of various steels during plastic deformation by measuring the dependence of impact strength on the amount of the preliminary plastic deformation.—V. G.

Photoelasticity. A. Mondina. (*Ing. Mecc.*, 1953, **2,** May, 9–16 ; June, 9–16 ; July, 25–29). [In Italian]. The author reviews the fundamentals of elasticity and optics, as both these subjects are essential to the understanding of photoelasticity. The instruments and procedures used in photoelastimetry are discussed with examples. The author shows how isostatic curves can be drawn and how, from isochromatic curves, it is possible to compute stresses. (15 references.)

Strain Gauge by Resistance Strip. I. T. Nishihara, H. Miki, and G. Naitō. (*Kyoto Univ., Bull. Eng. Res. Inst.*, 1952, **2,** Sept., 6–10). [In Japanese]. Satisfactory strain gauges were made by coating paper strips with bakelite-varnish containing carbon black, placed between silver-leaf terminals. Gauge length can be reduced to 0·5 mm., and the gauge factor is approximately 15.—K. E. J.

Brittleness in Steel Construction in Vehicles. V. Zignoli. (*Ing. Mecc.*, 1953, **2,** Mar., 5–8). [In Italian]. The causes of brittle fractures are examined. Failure of ductile materials caused by brittleness is studied, a theory of brittleness related to stress is put forward, and H. Schnadt's proposals are discussed.—M. D. J. B.

Theoretical Study of the Variation and Distribution of Stress Required to Cause Fatigue Failure with the Rate of Increase in Load as Used in the Prot Method of Testing. M. Davin. (*Rev. Gén. Méc.*, 1953, **37,** Feb., 49–54). A mathematical investigation is made of data obtained from the Prot type of fatigue test in order to obtain a theoretical explanation of the experimental results.—B. G. B.

Current Projects on Fatigue Properties of Materials. (*Proc. Amer. Soc. Test. Mat.*, 1952, **52,** 607–611). Over 80 projects being carried out in 30 American organizations concerning problems of fatigue of materials are listed.—B. G. B.

The Effect of Chromium Plating of Steel on the Fatigue Limit. G. M. Cabble, jun. (*Metal Finishing*, 1953, **51,** June, 106–108 ; July, 60–63). Trouble having been experienced through premature fatigue failure of chromium-plated locomotive side rods of nickel–chromium–molybdenum steel, fatigue tests were carried out on samples of the steel treated in various ways. The fatigue limits (in lb./sq. in.) of the various samples were as follows : (1) Untreated steel, 73,000 ; (2) plated with 0·003 in. of chromium, 57,500 ; (3) as (2) and baked at 440° C. (825° F.) for 45 min., 72,500 ; (4) as (2), buffed to remove the chromium and replated with 0·003 in., 50,500 ; (5) as (4) and baked as (3), 69,500.—J. P.

Critical Analysis of Shot Peening Results. A. Ferro. (*Ing. Mecc.*, 1953, **2,** Apr., 19–26). [In Italian]. After a brief review of the best shot-peening techniques, the author gives results of fatigue tests carried out on shot-peened components, particularly motor-car components. The author suggests criteria for the selection of suitable shot-peening procedure.

Vibration Damping. R. Plunkett. (*Appl. Mech. Rev.*, 1953, **6,** July, 313–315). Vibration damping is introduced and defined. A brief survey is made of 56 publications on the subject, under the headings : Vibration dampers ; connection damping ; material damping ; and vibration isolation.

Hardening Temperature for Hardening Tests on Case-hardening Steels. H. Kiessler. (*Stahl u. Eisen*, 1953, **73,** Aug. 13, 1116–1117). The answers to a questionnaire on the desirability of changing the temperature for hardening tests on unalloyed, chromium, chromium–manganese, and chromium–nickel steels are reviewed.—J. P.

Hardness Testing Plates. F. Flurschütz. (*Österr. Masch. Elektrowirtschaft*, 1953, **8,** July, 179–180). The author outlines the applications of hardness testing plates. The main causes of variations in hardness of the plates are discussed, including the effects of ageing ; plate specifications in use in various countries are given, followed by details of the German Standards.—L. D. H.

Methods of Measuring the Hardness of Materials in Different Directions. P. Grodzinsky. (*Rev. Gén. Méc.*, 1953, **37,** May, 147–152). The usual Brinell and Vickers methods of measuring hardness enable the resistance to deformation of a metal to be measured at a particular point, but do not allow variations in the hardness to be determined as a function of the direction of rolling. A survey is made of methods of determining this effect. Some results obtained are given.

Alloys with a Fixed Rate of Dilatation. (*Aciers Fins Spec. Franç.*, 1953, Mar., 82–85). The expansion of Fe–Ni, Fe–Cr, and Fe–Ni–Co alloys, and their applications, are discussed. Tables give the specific heats, thermal conductivities, Curie points, electrical resistivities, and melting points of several of these alloys, as well as their coefficients of expansion at 20°, 100°, 200°, 300°, 400°, and 500° C.—R. A. R.

An Investigation of the 'Composition/Heat-Resistance' Diagram for Quarternary Alloys of the Iron–Chromium–Nickel–Manganese System. I. I. Kornilov and K. A. Osipov. (*Izvestiya Akademii Nauk S.S.S.R., Otdelenie Khimicheskikh Nauk*, 1953, (3), 429–433). [In Russian]. The results of investigations of electrical resistance, hardness at room temperature, and resistance to plastic deformation at 800° C. of alloys of the above system are reported.—V. G.

Measuring Viscosity. (*Österr. Masch. Elektrowirtschaft*, 1953, **8,** Aug., 257–258). After dealing briefly with the principles of viscometry, and describing a number of methods of determining viscosity of fluids, the author describes the construction and mode of operation of a rotation viscometer.

Diffusion of Nitrogen in Iron. J. D. Fast and N. B. Verrijp. (*J. Iron Steel Inst.*, 1954, **176,** Jan., 24–27). [This issue].

Titanium Can Replace Manganese for Sulphur Control of Steel. J. D. Roach and R. S. Stewart. (*Iron Age*, 1953, **171,** June 4, 150–153 ; June 11, 126–128). Titanium as a desulphurizer is three times more effective than manganese but can only be used on killed steels, owing to its strong deoxidizing properties. Studies have shown that titanium can also be used to prevent strain ageing and grain growth, and a relationship has been established for the percentage of titanium needed as a partial replacement for manganese. Further advantages are the affinity of titanium for nitrogen and the formation of titanium carbides, which help to maintain fine grain characteristics at high temperature. However, the high cost precludes its use at present except as an emergency replacement.—A. M. F.

METALLOGRAPHY

A Thermodynamic Study of the Iron, Cobalt, and Nickel Sulphides. T. Rosenqvist. (*J. Iron Steel Inst.*, 1954, **176,** Jan., 37–57). [This issue].

The Application of Geiger-Müller Counters to X-Ray Spectrometers for the Direct Determination of Transformation Velocities. U. Rösler and W. Ruff. (*Alluminio*, 1952, **21,** Dec., 573–593). [In Italian]. A new method is described for the radiographic study of the kinetics of structural transformations at high temperatures by means of a Geiger-Müller X-ray spectrometer. The mathematical determination of the kinetic curves of the various phases in the transformations enables the velocity coefficients in the rate of transformation to be determined, as well as the mechanics of the phenomena. (25 references).—M. D. J. B.

Thermal Stabilization of Austenite in Nickel Steels. T. Ko and B. Edmondson. (*Acta Metallurgica*, 1953, **1,** July, 466–467). Further experimental work is reported on the stabilization of austenite above the M_s temperature. The authors conclude that there are some unknown factors controlling the stabilization.—A. D. H.

The Structure of Austenite at High Temperatures. I. A. Oding and M. G. Lozinskiĭ. (*Izvestiya Akademii Nauk S.S.S.R., Otdelenie Tekhnicheskikh Nauk*, 1953, (7), 1035–1043). [In Russian]. A method and apparatus for investigating the microstructure of austenite in steels during heating *in vacuo* are described. Some experimental results are discussed. After heating to high temperatures, flat blocks are formed in the austenite grains and their chemical heterogeneity is intensified, which is shown up by a dendritic or martensitic relief on the surface of a polished section. The preferential evaporation of metal during heating *in vacuo* is shown, not only locally in a geometric sense, but also by the changes in the chemical composition of alloys on the surface investigated caused by the different rates of evaporation of the atoms of the individual components.—V. G.

The Iron–Nickel–Nitrogen System. H. Muhlberg. (*Stahl u. Eisen*, 1952, **72,** Jan. 31, 197–198). In the γ' phase (Fe_4N) of the iron–nitrogen system the iron atoms can be replaced to a

considerable extent by nickel. Extending from the γ' binary field there is thus a γ' space extending far into the ternary system and running parallel to the iron–nickel side of the three-dimensional system. The γ' space ends at a low iron content as no nitride Ni_4N forms. The γ' space is wider than the γ' field. In the ϵ-phase (Fe_2N) of the iron–nitrogen system the iron atoms can also be replaced to some extent by nickel.—R. A. R.

The Effect of Dissociation Phenomena on Metal-Slag Equilibria, Investigated in the Fe–Cu–Al–S System in the Presence of Carbon. W. Oelsen, E. Schürmann, and H. Maetz. (*Z. Erz. u. Met.*, 1953, **6**, Apr., 128–137). The aim of this investigation and the experimental method are first briefly described. The dissociation phenomena in the Fe–Cu–S and the Fe–Al–S systems in the presence of carbon are described and their melting equilibria and slagging indices given. The effect of aluminium oxide on the slagging of the metallic sulphides (the Haglund method) is discussed, as is the desulphurizing effect of carbon and aluminium on carbon-bearing ferrous melts.

Decomposition of Iron Phosphide by Molten Zinc. R. Vogel and D. Horstmann. (*Arch. Eisenhüttenwesen*, 1953, **24**, May–June, 247–249). The equilibrium lines in the diagram of the Fe–P–Zn system at 750° C. have been determined metallographically. The lines show that iron has a greater affinity than zinc for phosphorus.—J. P.

Rational Phase Nomenclature. E. E. Thum. (*Metal Progress*, 1953, **63**, June, 136–144). An improved system of nomenclature for metallic phases proposed by a sub-committee of the American Society for Testing Materials is explained. The new system avoids the present indiscriminate use of Greek and Latin symbols and chemical formulæ.—B.G.B.

CORROSION

Studies on the Inhibition of the Corrosion of Iron by Solutions of High Acidity. C. C. Nathan. (*Corrosion*, 1953, **9**, June, 199–202). In *N* HCl, the inhibition of corrosion of steel strip and iron powder increases with molecular weight for a homologous series of amines. Steric factors which tend to favour adsorption of the amine on the metal also increase the inhibition efficiency. The amines investigated included the aliphatic amines, aniline and pyridine, their homologues and alkylated derivatives, and some dibasic aromatic amines.

Practical Limitations of the Use of Corrective Processes in Water Treatment. H. Herfeldt. (*Werkstoffe u. Korrosion*, 1953, **4**, June, 209–210). The use of an ion-exchange process to soften water may render the water corrosive ; for example, some processes yield water with an acid reaction. Further corrective treatment may, therefore, be necessary ; some of the difficulties that arise in this are described.—J. C. H.

Contamination of Condensate by Heat-Exchanger-Tube Alloys. J. D. Ristroph and E. B. Powell. (*Trans. Amer. Soc. Mech. Eng.*, 1953, **75**, July, 729–745). Results are presented from condensate contamination studies conducted at two steam power stations to evaluate the influence of temperature of condensate, gas content, and service time upon the metal contamination in steam condensate. Details are given of tests on 12 alloys including a stainless steel of the 18/8/2 Cr–Ni–Mo type.—D. H.

Influence of Organic Detergents on Metal Corrosion. T. K. Ross. (*Metal Treatment and Drop Forg.*, 1953, **20**, Apr., 183–187). The properties and structures of some of the more active agents encountered in commercial detergent preparations are discussed. In almost every case so far examined, detergents participate in corrosion phenomena, either protectively or destructively. Typical instances are given to illustrate the following methods of reaction : Increased activity of other agencies by means of superior wetting power ; direct reaction of the reagent with the metal ; adsorption of the metal surface so as to exclude other agencies and so give some degree of protection ; adsorption at the surface to give initial protection, followed by slow breakdown ; immediate or continuous attack of the metal by the adsorbed film ; and adsorption on corrosion products so as to modify their properties, thus affecting subsequent corrosion.—P. M. C.

Extending Hot Water Tank Life. R. L. Horst. (*Amer. Gas Assoc. Monthly*, 1953, June, 10–11, 50). The author discusses the electrochemical reactions likely to take place with anodic or cathodic protectors in hot water tanks. He gives graphs to show the beneficial effect of sacrificial magnesium anodes over a period of 400 days.

Water Treatment. W. J. M. Cook. (*Reports on the Progress of Applied Chemistry*, 1952, **37**, 42–50). Progress in water treatment during 1952 is reviewed under the headings : Coagulation ; Bacteriology ; Fluoridation ; Corrosion ; Boiler-feed Water ; Ion Exchange ; and General. (20 references).

Condensed Phosphates in the Treatment of Corrosive Waters. D. N. Parham and C. W. Tod. (*Chem. Indust.*, 1953, June 27, 628–631). The chemistry of condensed phosphates is considered and a historical survey of the use of metaphosphates for the prevention of scale deposition and corrosion is given. Experiments show that metaphosphates can inhibit corrosion in cold waters containing much chloride. The majority of condensed sodium phosphates are shown to be effective inhibitors on the basis of phosphorus content; the high efficiency of sparingly soluble sodium calcium metaphosphates is confirmed.—J. O. L.

Caustic Cracking in Steel Boilers—Use of Alkaline Phosphates for the Protection of Boiler Metal in Certain Cases of Stress Corrosion. R. Rath. (*Chem. Indust.*, 1953, June 20, 600–603). Experience of the value of trisodium phosphate in preventing corrosion in boilers with 20 years service at Gennevilliers, near Paris, is described. The influence of stresses and boiler water concentration are mentioned, and the lack of detailed knowledge of the corrosion mechanism emphasized.

Scale *vs.* Bare Steel Potential Differences May Explain Unusual Tank Vessel Corrosion. L. M. Mosher. (*Corrosion*, 1953, **9**, May, Topic of the month, 1–2). Recently an unusual pitting of the top surfaces of pipes and structural members has appeared in the bottom of ship's tanks carrying crude oil. It is suggested that galvanic corrosion occurs when the tanks have been cleaned and ballasted with sea-water.—J. F. S.

Self-Diffusion of Iron in Iron Oxides and the Wagner Theory of Oxidation. L. Himmel, R. F. Mehl, and C. E. Birchenall. (*Trans. Amer. Inst. Min. Met. Eng.*, 1953, **197**; *J. Met.*, 1953, **5**, June, 827–843). The authors have determined the rates of self-diffusion of iron in artificially prepared wüstites of various compositions, using the decrease in surface activity technique. Similar measurements are reported for artificial magnetites of nearly stoichiometric composition and for natural hematite single crystals. The data, together with thermodynamic data derived from the present study and from literature, are used to calculate rates of oxidation of iron and its oxides from Wagner's theoretical rate equations. Comparison with experimental data essentially confirms the Wagner theory, and the results are also consistent with the previously proposed transport mechanisms in iron oxides.—G. F.

The Influence of the External and Electrolytic Resistances on the Behaviour of Model Electrochemical Cells with a Readily Polarizable Electrode. W. Schwarz. (*Werkstoffe u. Korrosion*, 1953, **4**, June, 211–216). This theoretical dissertation on the effects of the internal and external resistances on the functioning of electrochemical cells includes a description of a method for determining potential/current curves for cells with a high internal resistance.—J. C. H.

Influence of Wetting Agent on Corrosion. IV—Protection under Acid Conditions. L. Piatti. (*Werkstoffe u. Korrosion*, 1953, **4**, May, 153–156). This proprietary wetting agent, which is the chlorhydrate of a mono-acyldiamine, is a good inhibitor of the corrosion of steel by hydrochloric acid. In a solution containing 22 g. of HCl per litre the attack is practically brought to a standstill by the addition of 1% of this compound.—J. C. H.

The Resistance of Autogenous Welds on Steel to Corrosion. E. Klosse. (*Werkstoffe u. Korrosion*, 1953, **4**, May, 172–178). Practical illustrations are given of the important effects of the design of welded parts on the resistance to corrosion of steelwork assembled by autogenous welding. This resistance depends so much on design, the nature of the basis metal and that of the weld metal, and the corrosive medium, that the behaviour of an actual welded structure cannot be predicted with confidence from laboratory corrosion tests.—J. C. H.

Protection against Corrosion by Sprayed Metal Coatings. H. Reininger. (*Werkstoffe u. Korrosion*, 1953, **4**, May, 156–172). This is a general review of recent literature on metal spraying. The subject is presented under two headings : (1) Reasons for unsatisfactory performance ; and (2) practical applications of sprayed coatings. (83 references).—J. C. H.

The VPI Rust Protection Process. W. Neukaus. (*Österr. Masch. Elektrowirtschaft*, 1952, **7**, June, 215–220). After a brief description of the chemistry of the VPI (vapour phase inhibitor) method of rust protection, the duration of protection given by different methods of application, with particular reference to impregnated VPI paper, is discussed.—H. R. M.

Notes on Reactive "Wash Primers" and Rusting-Resisting Media. B. F. H. Scheifele. (*Werkstoffe u. Korrosion*, 1953, **4**, June, 208–209). This is a note on the use of 'wash-primers' containing phosphoric acid, polyvinylbutyral resin, and zinc chromate, as a pretreatment for painting steel, galvanized steel, aluminium, and light alloys.—J. C. H.

Underground Corrosion of Galvanized Steel Pipe: Results of Study by U.S. Bureau of Standards. M. Lorant. (*Brit. Steelmaker*, 1953, **19**, Aug., 472–473, 485). Recent results obtained by the U.S. National Bureau of Standards confirm earlier work in showing that hot-dipped galvanized steel, having 3 oz. of zinc per square foot of exposed surface, is highly resistant to corrosion in many soils which are very corrosive to bare steel.—G. F.

Evidence of Corrosion Failures in Drill Stem Members. A. P. Farr. (*Corrosion*, 1953, **9**, Apr., 108–111). Measures taken to prevent corrosion of drill stems for oil wells are described and examples of corrosion fatigue failure are illustrated. Screw-threads are vulnerable zones and welding the tool joint to the pipe to prevent the mud from reaching the threads has proved a successful measure.—R. A. R.

Drill Stem Corrosion in West Texas. S. C. Moore. (*Corrosion*, 1953, **9**, Apr., 112—114). The costly failures resulting from corrosion fatigue of oil drill-collar joints and similar members have been mitigated by the use of magnesium rings.

The Corrosion Engineer Uses Plastics. F. L. Whitney, jun. (*Corrosion*, 1953, **9**, Apr., 123–131). Plastics may be conveniently divided into three major groups, elastomers, thermosetting, and thermoplastic materials. Examples of each are given with an outline of their most usual properties. A complex test piece for evaluating plastic coatings is described.

Bacterial Corrosion of Offshore Structures. J. A. Caldwell and M. L. Lytle. (*Corrosion*, 1953, **9**, June, 192–196). The cultivation of sulphate-reducing bacteria and their use in a laboratory test of various mud, sand, and clay media are described. Field tests with small steel panels were also used to determine the severity of bacterial corrosion of steel piling off-shore. Cathodic protection was a sufficient safeguard against the low rates found.—J. F. S.

Corrosion and Erosion in the Synthetic-Fuels Demonstration Plant. G. D. Gardner and J. T. Donovan. (*Trans. Amer. Soc. Mech. Eng.*, 1953, **75**, May, 525–533). Corrosion and erosion during two years of intermittent operation of the first American coal-hydrogenation plant are described. Isolated cases of local corrosion fatigue, caustic embrittlement and pitting are mentioned.—D. H.

A Method for Determining the Resistance of Insulating Joints and Pipe Line Coatings. H. F. Koester. (*Corrosion*, 1953, **9**, May, 159–162). Details of the calculations needed to convert observed to true resistances are given for insulated joints in buried pipes and the coating on the pipe itself. The procedures recommended have been used satisfactorily in New York.—J. F. S.

Hydrogen Blistering of Steel in Hydrogen Sulphide Solutions. T. Skei, A. Wachter, W. A. Bonner, and H. D. Burnham. (*Corrosion*, 1953, **9**, May, 163–172). Rates of transmission through the steel of the hydrogen formed by contact with saturated H_2S solutions were measured in the laboratory. Rates sufficiently high to cause blistering occurred, especially in the presence of alkaline cyanides. Frequent solution replacement increased the rate of transmission. The *p*H value had a marked effect. Air (2%) promoted transmission in acid solutions but inhibited it in alkaline ones.—J. F. S.

Corrosion-Resisting Cast Alloys Containing Nickel, Chromium and Molybdenum. M. M. Hallett. (*Soc. Chem. Ind. Chem. Eng. Group*, 1950, **32**, 39–50). The author traces and defines the influence of nickel, chromium, and molybdenum on the resistance to corrosion of five materials. These are 33%-Cr iron, Ni-resist., Corrosalloy S (stainless steel), Corrosalloy M (18–8 austenitic steel containing molybdenum), Corrosist B (Mo–Ni base alloy), Corrosist C (Ni–Mo–Cr base alloy). They were tested in various concentrations of nitric, sulphuric, and hydrochloric acids at various temperatures. The different corrosion susceptibilities are discussed in relation to the metallurgical properties of the alloys, particularly their microstructures.—J. C. B.

Research on Stainless Steels. Part III—The Passivity of the 18/8 Austenitic Steels. A. Ferri. (*Met. Ital.*, 1953, **55**, June, 203–207). After a brief discussion on passivity, the author examines the process, the surface conditions of the metal, and the crystallographic orientation. The author also describes the apparatus and research technique with which he demonstrates experimentally that passivity is a function of the tendency metals have to absorb oxygen or air. (20 references).

Corrosion Resistance of Titanium, Zirconium and Stainless Steel in Organic Compounds. I. R. Lane, jun., L. B. Golden, and W. L. Acherman. (*Indust. Eng. Chem.*, 1953, **45**, May, 1067–1070). Titanium, zirconium, and 20/29 Cr-Ni stainless steel are resistant to many organic acids and chlorinated hydrocarbons. Titanium can be attacked by formic, citric, and oxalic acids. Stainless steel is attacked by aniline hydrochloride solution, boiling acetic anhydride, and chloro-acetic and lactic acids. Zirconium is almost completely resistant to all compounds investigated, except some chloro-acetic acids. Zirconium and titanium will probably have wider applications than stainless steel in the organic chemical industry. (12 references).—K. E. J.

ANALYSIS

A Comparative Evaluation of Results of Determinations of Oxygen in Steels by Chemical and Vacuum-Fusion Methods. V. A. Mchedlishvili and A. M. Samarin. (*Izvestiya Akademii Nauk S.S.S.R., Otdelenie Tekhnicheskikh*, 1953, (3), 378–382). [In Russian]. The determination of oxygen in steels from the content and composition of non-metallic inclusions isolated by anodic solution of steel was compared with vacuum-fusion results. Agreement between these two methods is satisfactory, but when using vacuum-fusion, experimental conditions (time of fusion and temperature) should be adjusted according to the composition of the non-metallic inclusions.—V. G.

Mercury-Cathode Electrolysis and its Application to Steel Analysis. Methods of Analysis Committee. (*J. Iron Steel Inst.*, 1954, **176**, Jan. 29–36). [This issue].

Absorptiometric Determination of Cobalt in Iron and Steel. Methods of Analysis Committee. (*J. Iron Steel Inst.*, 1954, **176**, Jan., 63–66). [This issue].

Electronically Controlled Spectrographic Spark Source. A. Á. Bardócz. (*Nature*, 1953, **171**, June 27, 1156–1157). Circuit diagrams and details are given of two electronically controlled spark sources, one for high-energy sparks and the other for producing low-voltage condensed sparks and interrupted arcs. Methods of controlling the frequency of sparking in the two systems are discussed.—A. G.

New Method of Direct Quantitative Inorganic Paper Chromatography. S. V. Vaeck. (*Nature*, 1953, **172**, Aug. 1, 213–214). The method is based on the determination of the reflectance of the coloured spot at the wavelength of minimum reflectance, using a paper blank for a 100% reflectance standard. Factors governing reproducibility are discussed, and as an example, the determination of nickel in the presence of other metals is described.—A. G.

Automatic Apparatus for the Semimicro Determination of Oxygen in Coals, and More Generally in All Organic Products. A. Etienne. (*Chaleur et Ind.*, 1953, **34**, June, 157–158). A brief description is given of the apparatus, which comprises a fixed furnace capable of temperatures up to 1200° C. and a magnetic coil moving at controllable speed to push the sample into the furnace. For materials other than coal this coil is replaced by a moving furnace heated to temperatures between 400° and 900° C. and controlled by a time switch.—A. G.

A Semimicro Analytical Method of Determining Oxygen in Coals. C. Georgiadis. (*Chaleur et Ind.*, 1953, **34**, June, 159–162). The apparatus is for use in conjunction with the automatic apparatus described by A. Etienne, and details are given of nitrogen purification, reaction tube, transformation of CO to CO_2, method of adsorption, and the mode of operation.—A. G.

HISTORICAL

Henri Moissan, The Great French Electrometallurgist (1852–1907). (*Aciers Fins Spec. Franç.*, 1953, Mar., 126–128). His life and some of his researches are briefly outlined.

A Great French Metallurgist—Samson Jordan (1831–1900). (*Aciers Fins Spec. Franç.*, 1953, July, 76–79). A short biography of this metallurgist is presented.—V. G.

The Bog Iron of Loch Maree. J. E. Metcalfe. (*Mine Quarry Eng.*, 1953, **19,** June, 199–203). Evidence of the mining and smelting of bog iron ores in the North of Scotland is surveyed. The area supported the earliest iron industry in Scotland, but the most productive period was in the XVIIth century.—D. L. C. P.

Restoration of the First Iron Works. (*Wire and Wire Prod.*, 1953, **28,** May, 473–475). The Saugus Iron Works, near Boston, Massachusetts, which dates back to 1646, is being reconstructed with the financial support of the American Iron and Steel Institute. The story of the project of reconstruction is told.—J. G. W.

A Famous English Fireback of 1548. H. R. Schubert. (*J. Iron Steel Inst.*, 1954, **176,** Jan., 36). [This issue].

The Blacksmith in 17th Century England. H. R. Schubert. (*J. Iron Steel Inst.*, 1954, **176,** Jan., 70). [This issue].

The Woodscrew and Its Manufacture. K. Rennen. (*Draht, German ed.*, 1952, **3,** July ; *Wire and Wire Prod.*, 1953, **28,** Apr., 363–365). The development of woodscrew manufacture is traced and modern production is described.—J. G. W.

ECONOMICS AND STATISTICS

Work Preparation and Plant Management in a Steelworks with Ancillary Processing Plants. W. Preute. (*Stahl u. Eisen*, 1953, **73,** July 30, 1035–1041). When products other than bulk steel are made (*e.g.*, forgings and castings), plant management must take costs, prices, and market conditions into account. A careful balance is therefore necessary between technical and commercial considerations. The procedure for effecting this balance is described in detail and illustrated by several examples.—J. P.

Mineral Production Increases Again. H. McLeod. (*Canad. Min. J.*, 1953, **74,** Feb., 62–72). A detailed account of Canada's mineral production in 1952 and previous years is given. Iron ore production rose by 11% in 1952, due entirely to increased shipments from British Columbia. Exports of 3·8 million short tons included 700,000 tons to the United Kingdom.—A. G.

A Dynamic Programme for Conservation. J. R. Townsend. (*Metal Progress*, 1953, **63,** June, 79–81). Four ways in which conservation can overcome the current shortage of alloying elements in the U.S.A. are considered. Substitution by more common elements is estimated to be able to replace by 25 to 50% the civilian demand for scarce alloying elements. Reprocessing and redesigning of products, greater standardization, and the working of low-grade mineral deposits can all assist in overcoming the shortage.—B. G. B.

Western Germany's Iron and Steel Industry. (*Metal Bull. Special Issue*, 1953, June, 7–20). The activities of the West German iron and steel industry during the prewar, war, and postwar years are reviewed. The splitting up of the large combines and the dismantling of equipment for reparations has resulted in great changes in the industry and these are discussed.—B. G. B.

Steel Industry Progress in Eastern Germany. (*Metal Bull.*, 1953, July 28, 7–10). An attempt is made to review the progress of the East German steel industry in the past few years. Eastern Germany is very dependent on the import of high grade iron ores. Pig iron production in 1952 was 573,000 tons. A short account of the activities of seven of the major firms is presented.—B. G. B.

International Efforts to Increase Productivity. K. P. Harten. (*Stahl u. Eisen*, 1953, **73,** July 30, 1009–1013). The author surveys the development and activities of organizations dealing with improvement of productivity, and then discusses the functions of the International Labour Office in Geneva, the Organization for European Economic Co-operation, and the tasks before the newly established European Productivity Agency in Paris.—J. P.

MISCELLANEOUS

Man, Metals, and Power. N. L. Mochel. (*Proc. Amer. Soc. Test. Mat.*, 1952, **52,** 691–731). The first section deals with the life and work of H. W. Gillett. He was the first director of the Battelle Memorial Institute and chief technical advisor from 1934 until his death in 1950. In the second section the use of metals in the construction of steam turbines and allied equipment is discussed in some detail.—B. G. B.

Modern Conception of Warehouse for Special Steels. (*Acier Fins Spec. Franç.*, 1953, Mar., 45–50). The importance of the existence of a network of depots for the sale of special steels is stressed. The organization of such a depot is described.—V. G.

Dust Removal by Suction and Dust Separation in the Metal Working Industry. H. Mürmann. (*Metall*, 1953, **7,** Oct., 779–784).

BOOK NOTICES

HART, CYRIL E. "*The Free Miners of the Royal Forest of Dean and Hundred of St. Briavels.*" With Foreword by Rev. F. W. Potto-Hicks. 8vo, pp. xxi + 527. Illustrated. Gloucester 1953 : British Publishing Co., Ltd., (Price 21*s.*)

The author is one of Her Majesty the Queen's Verderers of the Forest of Dean in Gloucestershire, who previously has written several historical essays on various subjects concerned with Dean Forest, of which his history of gold-mining is of particular interest. By these essays he has given ample proof of his qualification for writing the history of iron-ore and coal mining in the Forest, and of the ancient and still surviving institution of the free miners. Extensive research work, principally in the vast historial collections preserved at the Public Record Office in London, enabled the author to produce a most completely documented historical work which for this reason alone is of very great value. Never before has so much documentary evidence been published, and every reader interested in the history of mining and ironmaking will be grateful for it, although the author modestly presumes that general readers may wish to pass lightly over the more detailed portions primarily intended for the use of the free miners and other inhabitants of the Forest and its vicinity. The extensive depositions, principally by witnesses who lived in the Forest area in former centuries, enlarge our knowledge to a considerable extent. They will be greatly appreciated and read with interest, because they make an immediate contact with the past and revive the picture of persons who lived in a now remote age, their views on the various questions concerned and their ways of expressing them.

In Hart's book the historical development of mining in the Forest is traced back to the very early beginnings in the era of the occupation of Britain by the Romans ; they knew and worked the iron-ore deposits, but the actual labouring was done by the subjugated British miners. In the Middle Ages the Forest of Dean was a main centre of ironmaking from which the English kings in their various wars in France, Ireland, and Scotland obtained war materials, and also miners who undermined the walls of fortresses, and smiths for the forging and repairing of weapons, utensils and the iron parts of catapults which were the fore-runners of cannon. After 1612, at which date the blast-furnace was introduced in the Forest of Dean, the area again became one of the most important centres of ironmaking in England and remained so during the seventeenth and eighteenth centuries. In the same period large quantities of the hematite iron-ores of the Forest and of cinders left from medieval ironmaking were transported into other regions, as far as Ireland and Lancashire, greatly assisting the development of the iron industry in these areas by supplying high-grade ores and fluxes.—J. R. SCHUBERT

HULTGREN, RALPH. "*Fundamentals of Physical Metallurgy.*" 8vo, pp. xiii + 395. Illustrated. New York, 1952 : Prentice-Hall, Inc. London. 1953 : Macdonald & Co. (Publishers), Ltd. (Price 70*s.*)

There are two surprises awaiting people who read Dr. Hultgren's book : The price and the title.

The chapter headed " Introduction " is the most interesting section of the book. In it the author's views on the relation of the science of metals to the practice of metallurgy, and the proper place of these studies in a university curriculum, are set out clearly and entertainingly. The views are refreshingly modern, although, in part, original to the point of heresy. For example : " Physical Metallurgy is unique in that the science of metals, on which it is based, was developed mostly by physical metallurgists and many

parts of this science are little known in the departments of pure science." (This is true in the United States but not in Europe).

The author chooses to define physical metallurgy as all metallurgy other than that concerned with the extraction of metals from their ores. Consequently, a person who sets out to equip himself as a "physical metallurgist" faces the task of acquiring a familiarity with an enormous body of factual and descriptive information on the metallic state. Two approaches can be highly recommended. One, which may be called the encyclopaedic method, is to study the A.S.M. "Metals Handbook," the other, intellectually more satisfying, is to digest "Metals" by Carpenter and Robertson; to someextent the two methods are complimentary. A student embarking upon a task of this magnitude can derive a great deal of value from first reading a simple survey of the whole field. For this purpose Dr. Hultgren's book is admirable. The threads of reasoning which permeate the whole are clearly defined and the student is provided with a panoramic view of the subject matter. The book could have been sub-titled "A Young Person's Guide to Metals and Metals Handbook."

All this, excellent as it is, seems to bear little relation to the title or the sentiments, concerning the science of metals, expressed in the Preface and Introduction. The word "Fundamentals" and phrases such as "This book presents these scientific principles . . ." might suggest that the book is concerned with the important theories of the physical chemistry of metals. Perhaps this view is too narrow. It may be that they are intended to imply that the book is concerned with the phenomenological bricks from which the classical metallography is built—such subjects as phase relationships, diffusion, nucleation, dislocations, etc. In fact, the book contains much factual and descriptive information, some sketchy treatments of basic phenomena and a sprinkling of physical-chemical theory. In general, the ingredients are smoothly blended, but there are some lumps in the pudding. For example, four pages are devoted to an ingenious derivation of the phase rule (introducing fugacity along the way!) but no other thermodynamic concepts appear. This lavish treatment of the phase rule is even more surprising when it is realised that the martensitic reaction is dismissed in less than half a page.

It is to be hoped that no student will be intimidated by the author's warning that some of the problems require a good background in physics and chemistry and can be omitted. They are all very elementary, sometimes trivial, but often illuminating.—WALTER S. OWEN

KEYSER, CARL A. "*Basic Engineering Metallurgy. Theories, Principles and Applications.*" 8vo, pp. x + 384. Illustrated. New York, 1952 : Prentice-Hall, Inc. ; London, 1953 : Macdonald and Co. (Publishers), Ltd. (Price 60*s*.)

The author of this book is Associate Professor of Metallurgical Engineering at the University of Massachusetts. He has prepared the book mainly for engineering students who study metallurgy. The treatment can be regarded as falling under two headings. In the first place, there are a number of chapters covering the principles of engineering metallurgy and on phase changes in iron and steel and the effects of the alloying elements in steel, together with general accounts of the properties and uses of the non-ferrous metals. Secondly, the various shaping and fabrication processes are discussed, as well as heat-treatment operations and the equipment used, providing a useful and interesting introduction to the broad field of the preparation of metal for service. The treatment of this aspect seems to be usual in American books ; in comparison, in British books it is, unfortunately, not so strongly featured.

The writing is good, and clearly expressed, but, to the reviewer, the treatment of principles, in particular of alloy structure, in some way lacks coherence, and it does at times imply a greater familiarity with physical chemistry than is possessed by the more practical kind of engineering student. Undoubtedly, this tendency has arisen because of the author's praiseworthy attempt to maintain a fresh approach and not to make the subject too heavy going.

Nevertheless, there are one or two specific points to which the reviewer would draw attention. It goes without question that, in expounding the principles of engineering metallurgy, the nature and properties of the three metallic constituents, pure metals, solid solutions, and intermetallic compounds, must be clearly distinguished and compared. Yet in this book there is no general discussion of compounds, nor of equilibria involving them. As far as can be seen such a constituent is first encountered in the discussion on steel, where iron carbide is summarily dismissed as a chemical compound. Further, in the chapter on equilibrium diagrams the author covers the solid solution and eutectic type diagrams and also deals with the peritectic reaction, but he makes no mention of the eutectoid, which comes sharply at the reader in the chapter on phase changes in iron and steel.

At the end of each chapter there are a number of questions and problems. These are not necessarily full-length examination questions and may only require very short answers.

In general, the book is a useful and interesting introduction to engineering metallurgy, although it should be made clear that it does not set out to supply the detailed engineering metallurgy of individual alloys. The volume is very attractively produced, but the price compares unfavourably with those of British books: a well-known British book on engineering metallurgy sells at less than one-third of the price of the book under review.—A. R. BAILEY

KIEFFER, R., and P. SCHWARZKOPF. "*Hartstoffe und Hartmetalle.*" Unter Mitarbeit von F. Benesovsky und W. Leszynski. 8vo, pp. xvi + 717. Illustrated. Wien, 1953 : Springer-Verlag. (Price 136*s*.)

This is a most excellent book. The progess in the technology of hard metals in recent years and in the basic knowledge concerning them has been so rapid, and the information scattered so widely in the literature, that the issue of a collective work was well overdue, and, although some treatises on powder metallurgy contain brief chapters on the subject, the book under review is far more comprehensive, and is important in filling a real need. Furthermore, the authors are themselves two of the leading experts in hard-metal development, in which they have been largely instrumental, so that no more authoritive source could be desired.

The work consists of two parts. The first, on "Hard Substances," presents the fundamental requirements and properties of hard compounds, which include the carbides, nitrides, borides, and silicides of the transition metals of the 4th, 5th and 6th Periodic Groups ; those of thorium and uranium are also briefly dealt with, and so are non-metallic and natural hard materials, though less fully. The classification follows systematically that of the Periodic Table, and, after a short but lucid historical survey, the theory of hard interstitial compounds is discussed from the point of view of atomic and electronic structure, and its bearing on bond strength and other crystal-physical properties. This is followed by a chapter each on the carbides, nitrides, borides, and silicides. The methods of manufacture are reviewed, with numerous practical data and references ; then each individual compound is dealt with at length in separate sections covering the respective metal/non-metal system, properties, applications, and any special features of the phase. Further, the multiple carbide (nitride, boride, silicide) systems, in their various combinations, are excellently discussed from the viewpoint of solubility, properties attained and potential applications. Particularly interesting is the information on borides and silicides, some of which has only advanced to practical eminence through quite recent researches. The first part concludes with a valuable chapter on non-metallic hard compounds (diamond, silicon carbide, boron carbide, corundum), and a useful comparison is given of their properties with those of the hard metals.

The second part, on "Hard Metals," deals with the practical alloy products obtained from the above as raw materials, with and without binder addition. An illuminating historical survey of the development of various commercial brands (and of materials which had remained in the research stage) is given, presenting at the same time a guide to the copious patent literature. Such a bird's-eye view of a subject, which, in its rapid and often rather too empirical growth (largely behind locked doors) has assumed great complexity, seems especially appropriate.

The practical processes involved in hard-metals technology are described, followed by a comprehensive section on the physics of sintering and on the diffusion mechanism in such

systems as WC–TiC–Co. Hot-pressing and infiltration techniques are also well dealt with. A section on the testing of hard metals (hardness, density, etc.), and one on properties in the many combinations and permutations of materials, are illustrated by valuable diagrams and tabulated data. The authors' presentation here has particularly the merit of clarity and system, in a field which is so easily obscured by less essentials.

Two chapters follow on the applications of hard metals to wear-resistance problems (*e.g.*, mining tools, wire-drawing dies, etc.), and to cutting tools and machinability questions, dealing admirably with both the theoretical and the applied aspects.

The last section, on "High Temperature Materials," is probably of the most immediate present-day interest in relation to gas-turbine materials. Its 64 pages are almost self-contained, and could profitably have merited issue as a separate booklet, combined with some data from Part I. Again, the historical and physical background is fairly presented, leading to the modern TiC-base compacts, as well as the yet more recent boride-base ones, claimed to be to some extent superior.

The recent researches into the use of silicides (such as $MoSi_2$) as protective coatings for high-temperature applications find prominent mention. The results to date of these investigations are presented, while those on other carbide-, nitride-, boride-, and sulphide-base products are set out in as much detail as can be said to be known ; the account extends also to recent metal-ceramics progress, to which a brief but, in this context, adequate section is devoted, and a final note outlines the authors' assessment of the more promising future developments in this field.

The book is well planned, well written, and well produced, and, apart from the wealth of correlated data that it gives, should not fail to stimulate much new thought and investigation.—H. J. GOLDSCHMIDT

JONES, E. B. "*Instrument Technology.*" Volume I. "*Measurement of Pressure, Level, Flow and Temperature.*" La. 8vo, pp. xii + 315. Illustrated. London, 1953 : Butterworths' Scientific Publications. (Price 35*s.*)

This book deals with that side of instrument technology with which the iron and steel industry is particularly interested, and it gives in a clear manner examples of the various instruments used for measuring such variables as pressure, temperature, rate of flow, etc.

If it had done nothing else, the author could have been thanked for having brought together data normally found in the catalogues of the various instrument manufacturers and connected documents, and therefore for saving the time of those concerned with instruments who are interested in the data.

When, however, the author hopes that his book will more than cover the requirements of the Intermediate Examination in Instrument Maintenance of the City and Guilds of London Institute, which is intended for the training of maintenance personnel capable of completely overhauling the instruments, he shows a lack of appreciation of the requirements, as nowhere in the book, except in a very sketchy form, does he touch upon such subjects as source of errors, prevention of common faults, systematic fault finding and correction, etc. It is to be hoped that in the Volume II, to follow, he will bear this point in mind.

The contents of the book, examined in detail, could be criticized in a number of places. The following examples are simply picked up at random from, unhappily, a relatively large number which cannot fail to strike anyone looking at the book with some practical knowledge.

In the section on "Measurement of Flow—Pressure Differential Methods," p. 133, it is rather useless to give a mixture of practical pressure tappings without making reference to where the corresponding flow coefficients are to be found. The author could at least mention that two of the types are recognized by B.S.1042, and that the coefficients applying to those can be found in that code.

Table V, p. 209, in the Section on "Change-of-state Thermometers," gives resetting of the pointer as a means of correction for the difference in level of the bulb and Bourdon tube of vapour-pressure thermometers. This can be dangerous advice.

One wonders why, in the same Table, the specification of accuracy of the three types of dial thermometer does not follow B.S.1041, and why, in the reference to pyrometric cones on page 210, it is only stated that they must be heated at a controlled rate when, in fact, it is also necessary for the atmosphere to be controlled if the accuracy given is to be relied upon.

In conclusion, the book would have gained appreciably had the author acquainted himself more positively with the practical side of instrument technology.—NEIL H. TURNER

SCHACK, ALFRED. "*Der industrielle Warmeübergang.*" Für Praxis und Studium mit grundlegenden Zahlenbeispielen. 4., neubearbeitete und erweiterte Auflage. 8vo, pp. x + 400. Illustrated. Düsseldorf, 1953 : Verlag Stahleisen m.b.H. (Price DM 38·50).

This comprehensive work on industrial heat transfer is the fourth and enlarged edition of a book the third edition of which appeared as recently as April, 1947. The author points out that since that time a number of important publications concerning heat transfer have appeared in America and in England, and these have been incorporated, often in a simplified form, in the present edition.

The first short Section is of an introductory nature and briefly mentions the three main modes of heat transfer, namely, conduction, convection, and radiation. Section B is the longest and probably most important part of the book, and deals comprehensively with heat transfer by conduction, convection, by the condensation of vapours, and by radiation. Section C, scarcely less important than Section B, is concerned with calculations concerning exchange systems both with and without recuperation.

The mechanism of heat transfer during industrial heating is the subject matter of Section D. Section E deals with pressure drop in tubes and the like, and Section F with the relation between pressure drop and heat transmission.

Section G considers a number of practical heat transmission problems, commencing with the simple case of the transmission of heat through a wall of known heat conductivity and surface temperatures. An interesting problem considered by the author is that of a wall of known thickness and heat conductivity which must be so insulated that with a stated inside temperature the heat losses shall not exceed a certain specified value. He considers the question of what type of insulation to use, how thick it must be, and what temperatures will be reached on the outside.

In Section J is to be found a number of tables giving the conductivity, specific gravity, etc., of a large number of materials.

The book concludes with 118 references, from which it is obvious that the author has referred extensively not only to the literature of his own country but also to that of other countries, particularly England and America. There are two indexes, *viz.*, a name and a subject index, and both are adequate.

It is impossible to speak too highly of this comprehensive work. The style of writing adopted by the author is one that anyone with a general knowledge of the subject of heat transmission would be able to follow even if his knowledge of the German language were somewhat limited. The book is well printed and bound and it will not be surprising if this fourth edition will shortly be followed by a fifth edition.

J. FERDINAND KAYSER

TIMOSCHENKO, STEPHEN P. "*History of Strength of Materials.*" With a brief account of the history of theory of elasticity and theory of structures. 8vo, pp. x + 452. Illustrated. New York, Toronto, London, 1953 : McGraw-Hill Book Co. Inc. (Price 71*s.* 6*d.*)

To attempt to write a history of the strength of materials and the theory of elasticity requires both immense knowledge and great courage. Knowledge, because a balanced and authoritative assessment of the real contribution made by the many mathematicians, scientists, and engineers who have worked in this field over the past 300 years is a difficult task for any man ; courage, because the three-volume work of Todhunter and Pearson "A History of the Elasticity and Strength of Materials" has remained to the present day the standard work, and a new text is sure to be compared with it.

Timoshenko is probably one of the few living authorities who could undertake such a task and it can be said, without hesitation, that he has reached a very high level of achievement in his book. He has been very objective in

his record and has given due credit to the host of writers and investigators.

Todhunter and Pearson brought the account up to the 1890's and Timoshenko's more concise account of the early years can well be supplemented by a study of the more extended treatment of Todhunter and Pearson. Timoshenko's book, however, is invaluable in summing up the main contributions made by the older elasticians and in giving an insight into their lives and the circumstances which brought them into the field. The soundness of Timoshenko's assessment of the more recent developments must, however, be put to the test of time before a judgment can be given, but, viewed from the present time, it is thought that few will quarrel with his later chapters. In his preface, Timoshenko mentions that " progress in strength of materials cannot be satisfactorily discussed without considering the development of the adjacent sciences such as the theory of elasticity and the theory of structures ". The only possible criticism of this excellent work might be that in assessing the progress the advances in practical engineering must also be considered. Timoshenko notes the backward state of the subject in England in the early part of the nineteenth century, but it must be remembered that it was at this time that England was making the outstanding advances in the practice of engineering, particularly in relation to the steam engine, to railways, and to the development of metals and machinery generally. To read for example of Watt's difficulties in obtaining the right materials and workmanship for his engines is to see how much was contributed by such men. Timoshenko has noted this circumstance, but is of the opinion that " this experimental approach did not contribute much to the general theory of strength of materials . . ."

The teaching of strength of materials in universities and colleges has tended to become somewhat stereotyped in the last twenty years, and it is believed that a study of sources of knowledge in this field could do much to enliven and recast teaching generally. In particular, therefore, Timoshenko's very readable and reliable history can be profitably studied by all those who engaged in teaching. It arouses a curiosity and desire to read more widely. This book should be a personal possession of every engineer who is studying or teaching strength of materials. Its price is its only disadvantage.—HUGH FORD

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